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THE SPECTROSCOPIC LABORATORY OF THE SOLAR OBSERVATORY[1]

By GEORGE E. HALE

An important requirement in the programme of research of the Solar Observatory is met by the provision of a spectroscopic laboratory, adequately equipped for the investigation of such physical and chemical phenomena as may be encountered in connection with our solar and stellar observations. It will only occasionally happen that data required to explain the results obtained with the solar spectrograph and the spectroheliograph, are already available in spectroscopic literature. The Zeeman effect, for instance, has been recorded in the case of comparatively few lines, so that without additional observations it could not be determined whether certain lines which vary together in the Sun, also behave alike in a magnetic field. Displacements due to pressure must frequently be known in connection with measurements of lines in the solar spectrum, but the required values are only occasionally found in published papers. The same may be said of the effects of change of temperature, of potential, of self-induction, of current strength, of the influence of the gaseous atmosphere in which the luminous source is placed, etc. It is evident that what is essential, in case the results constantly encountered in both solar and stellar

[1] *Contributions from the Solar Observatory*, No. 10.

work are to be interpreted without delay, is a collection of light-sources so designed and arranged that the effect of any of the above mentioned variables can be observed with spectroscopes of any desired resolving power.[1] It is not so much a question of the saving of time, which the provision of these means undoubtedly offers, as it is of the greatly increased efficiency of the working programme thus rendered possible. The immediate imitation in the laboratory, under experimental conditions subject to easy control, of solar and stellar phenomena, not only tends to clear up obscure points, but prepares the way for the development along logical lines of the train of reasoning started by the astronomical work. It is a question, then, of equipping the laboratory in such a way that its various resources may be effectively utilized at any time, and without the delays ordinarily experienced when apparatus must be specially prepared for a certain investigation. In the desired plan the apparatus must be always ready, needing only the operation of a switch or the adjustment of a mirror to bring it into action.

In the spectroscopic laboratory of the Yerkes Observatory I first tried the principle which has been more fully developed in our spectroscopic laboratory on Mount Wilson. The various light-sources, including an ordinary arc in air, a spark in air, a spark in liquids, and a spark in compressed gases, were arranged on the circumference of a wooden table, having at its center a plane mirror capable of rotation about a vertical axis. By means of this mirror, set at the proper angle, light from any one of the sources was reflected to a concave mirror which, in its turn, formed an enlarged image of the light-source on the slit of a concave grating spectrograph.

At the Solar Observatory the apparatus is arranged as shown in Plate I. Instead of a circular wooden table, an annular concrete pier is employed, giving space on the inner wall for the various switches used to control the current supplied to the different sources, and also permitting the observer to inspect any light-source from the direction of the plane mirror at the center of the pier. Instead

[1] As an illustration of this it may be remarked that in our study of sun-spot spectra the following light-sources have been employed: ordinary arc, in air and in CO_2; rotating arc, at low and high pressures; synchronous arc; spark in air; spark in water; oxyhydrogen flame; electric furnace.

of a single plane mirror, two are provided, capable of rotation independently of one another, about the same vertical axis. By means of divided circles, the azimuth of either mirror can be read. When the Littrow spectrograph[1] is in use, only the lower plane mirror is employed. By setting this at the proper angle the light from any one of the sources can be sent to the concave mirror (seen near the the middle of Plate I), which forms an image of the source on the slit of the Littrow spectrograph. If the one-prism quartz spectrograph, the interferometer, or the echelon spectroscope is to be used in place of the Littrow spectrograph, for the study of the light-source, the concave mirror is tipped back at a small angle, so as to return the light to the upper plane mirror, from which it is reflected to the slit of one of these instruments. In Plate I the quartz spectrograph may be seen just above the concave mirror. To the right of this is a Hilger one-prism spectroscope, which provides a monochromatic beam for observation with the interferometer (shown in position near the spectroscope), or with the echelon spectroscope, which stands on the right of the pier that carries these instruments. This pier is separated from the annular pier by a space through which the observer may pass.

The various analyzing instruments, with which the light-sources are studied, may be briefly described as follows:

1. A direct-vision spectroscope by Jobin, for the preliminary visual examination of spectra.

2. A Fuess quartz spectrograph, with collimator of 3.8 cm aperture and 81.3 cm focal length, and camera of the same aperture and focal length. This instrument has a double Cornu prism of quartz, and a Zeiss prism of ultra-violet glass, to be used if somewhat higher dispersion is desired. The spectrograph is provided with means for photographing a series of narrow spectra on a single plate, and is used for preliminary and for qualitative studies, especially in the ultra-violet.

3. A Littrow spectrograph of 12.5 cm aperture and 3.72 m focal length. The combined camera and collimating lens is by Brashear, and is corrected for work in the visible spectrum. The

[1] The rectangular box which carries the slit and plate-holder of this instrument is shown on the pier at the left of Plate I.

plane grating, by Michelson,[1] has a ruled surface 8.3×4.4 cm, with 7,000 lines to the cm. It may be used in any order, by setting it at the proper azimuth. The slit is mounted immediately above the photographic plate. The plate-holder can be raised or lowered, so as to permit several spectra to be photographed on a single plate.[2]

4. A Michelson interferometer (not shown in the plate), for the analysis of spectral lines, the determination of absolute wave-lengths and the measurement of lengths. This instrument receives monochromatic light from a one-prism spectroscope by Hilger, provided with a prism of special form, from which the beam emerges at an angle of 90° with the axis of the collimator. Different parts of the spectrum can be brought to the slit of the interferometer collimator by rotating the prism. The same spectroscope can be used in connection with a Pérot-Fabry interferometer or with an echelon spectroscope.

5. A Pérot-Fabry interferometer by Jobin, exactly similar to the instrument used by Messrs. Pérot and Fabry for the determination of absolute wave-lengths and the analysis of spectral lines.

6. A 33-plate echelon spectroscope by Hilger, with plates 15 mm thick. This instrument is used in studies of the Zeeman effect, and other work requiring the highest obtainable resolving power. The slit can be opened or closed from the eye-end, or moved entirely out of the way when a spectral line is being picked out for observation. In the latter case the echelon is moved to one side and the image of the spectrum, formed by the auxiliary spectroscope in the focal plane of the collimator of the echelon spectroscope, is seen with the observing telescope. Provision is made for using the echelon at 90° from its ordinary position, as Nutting has done, for the purpose of separating the overlapping spectra. For spectra having but few lines it is sometimes advantageous to remove the prism from the auxiliary spectroscope and insert it beyond the echelon. When this is done the observing telescope stands at 90° with the axis of the echelon, as shown in Plate I.

[1] We are indebted to Professor Michelson for the use of this excellent grating, which is one of the first products of his new ruling engine.

[2] This temporary instrument will be replaced by a permanent one of 5.5 m focal length.

The following apparatus stands on the annular pier: The first instrument on the right is a DuBois magnet of Hartmann & Braun's larger model, for studies of the Zeeman effect. It is mounted on a base in such a way that it can be rotated through an angle of 90°, so that light from the source can be observed parallel or at right angles to the lines of force. A bismuth spiral is provided for measuring the strength of the field. In the illustration a mercury tube is hung between the poles of the magnet, and connected by heavy pressure tubing with the Geryk duplex vacuum pump shown on the wooden table at the right. The magnet requires a potential of 64 volts, which is supplied from a storage battery in an adjoining building. The vacuum pump, which is supplied with a McLeod gauge by Müller-Uri, is driven by a small electric motor. A transformer of 600 watts capacity, giving from 6,000 to 10,000 volts, is used to illuminate the mercury tube. This is supplied with an alternating current from the generator in the power house. In connection with the transformer there are provided a condenser of variable capacity, and a coil of variable inductance.

Just beyond the magnet may be seen the apparatus for the study of the spark spectrum in air, at atmospheric pressure. The metals to be investigated are held by a pair of clamps in the lower set of terminals. The upper terminals are in series with the lower ones and serve as an auxiliary spark-gap. An electric fan, blowing a strong current of air upon the two sparks, prevents arcing and undue heating of the poles.

To the left of the air spark stands the apparatus for the study of the spark spectrum in water and other liquids. This consists of a strong iron case, into which the horizontal terminals are led through long corrugated cylinders of vulcanite. Glass windows, in the front and rear of the case, permit the spark to be seen from either side. The metals to be investigated are turned or ground into the form of small rods, and are mounted in brass caps, which can be screwed as terminals to the rods passing through the vulcanite cylinders. These rods are threaded, permitting the distance between the terminals to be varied at will. As the poles are rapidly consumed during the passage of the spark, it is necessary to adjust the distance between them while the exposure is in progress. For

this purpose a gear is attached to the rod carrying one of the terminals (the left one in the illustration), and this can be turned by means of a pinion at the inner extremity of a long ebonite handle, mounted on a conical ebonite support attached to the iron case. By this means the distance between the poles can safely be controlled, even when a transformer giving 64,000 volts is employed. When water is used it is kept circulating through the tank during the exposure, entering by means of a rubber tube near the bottom of the tank, and passing out through a rubber tube at the top. An auxiliary air-spark, blown out by the electric fan, is always used in series with the water-spark. The voltage, self-induction, capacity, etc., of the discharge circuit can be varied as desired. A tight-fitting iron cover is provided for the tank, in case high liquid pressures are to be used.

To the left of the central plane mirrors may be seen the ordinary arc, for experiments at atmospheric pressure with carbon or metallic poles. This arc is provided with an automatic regulator, so constructed as to keep the poles well separated during the exposure. By means of a suitable rheostat, the current through the arc can be varied as desired. Important differences in metallic spectra are obtained by the use of currents of 2 amperes and 30 amperes respectively, the difference of potential between the poles remaining the same in each case. Direct current of any desired voltage, up to 110, is applied to this arc from a storage battery, and alternating current, of one, two, or three phase, from the generator in the power house.

The next light-source on the pier is a synchronous rotating arc designed by Professor Crew, and constructed for us under his kind supervision. It consists of a small alternating motor, with a device for bringing it into synchronism with the single phase alternating current from our generator. By means of a position circle the rotating metallic electrode can be set at any desired angle, so as to permit the arc to be observed at any phase from 0° to 90°. The fixed electrode is adjustable by means of a hand-screw. The interesting variations in arc spectra obtained by varying the phase have been described by Professor Crew in the *Astrophysical Journal.*[1]

[1] **22**, 199–203, 1905.

Next to the synchronous arc stands the pressure arc, for the study of the low potential discharge (up to 110 volts, direct or alternating current) in various gases at low and high pressures. This apparatus was constructed by Gaertner. The rotating arc is viewed through a window in the front of the case. One of the electrodes can be adjusted, if necessary, during the exposure. Pressures up to 60 atmospheres are supplied from cylinders of liquid CO_2, obtained in Los Angeles. For higher pressures a special pump, kindly designed by Mr. Petavel of the University of Manchester, and constructed under his supervision by Charles W. Cook, the University instrument maker, will soon be installed. For low pressures the Geryk pump is used.

All investigation on the details of the solar image are made with the aid of the Snow telescope. Sunlight is nevertheless frequently required in the laboratory for comparison spectra, etc., and is supplied by the Fuess heliostat shown on the shelf outside the window, on the right of the plate.

The switch-board, with connections to the power house and storage battery, is shown on the left of the plate. Ammeters and voltmeters for direct and alternating current are provided. A large 5 K. W. transformer, specially built by the Peerless Electric Company, giving 1,000, 2,000, 4,000, 8,000, 16,000, 32,000 or 64,000 volts, will soon be installed.

A Ducretet coil, giving a 35-cm spark, with rotating mercury interrupter, has recently arrived. This will be used for various purposes, and with an X-ray tube for certain investigations on ionization. A sensitive radiometer, built by Gaertner, and fitted by Professor Nichols with a suspension system which he was kind enough to make for us, is also available.

Our recent study of sun-spot spectra has made it necessary to supplement the above equipment with a Moissan electric furnace, of 50 K. W. capacity. This is being installed, with a large Littrow spectrograph, in our Pasadena laboratory, since the power plant on Mount Wilson cannot supply sufficient current. The 5 K. W. high-potential transformer will also be used for the present in Pasadena.

It is not the purpose of this article to describe in detail the other rooms of the laboratory, which include a plate-measuring room,

with a stereocomparator and other measuring machines for the study of photographs of spectra and spectroheliograph plates; an enlarging room, with cameras for use with skylight or electric arc; two photographic dark rooms; a clock room, containing a Riefler mean time clock, with nickel-steel pendulum, which controls electrically a mean time clock in the Snow telescope house; a small chemical laboratory, etc. The laboratory is heated by steam and lighted by electricity.

SOLAR OBSERVATORY,
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SUN-SPOT LINES IN THE SPECTRUM OF *ARCTURUS*[1]

By WALTER S. ADAMS

The spectrum of *Arcturus* has always been of considerable interest to those investigating the subject of stellar classification, because of its intimate relationship to that of the Sun. Certain differences have, indeed, been recognized,[2] but since the study of its spectrum, as in the case of most other stars, has been confined almost wholly to a limited region in the blue portion photographed for the purpose of determinations of radial velocity, it has not been possible to establish any very definite relationship with other stars or with the Sun.

In connection with some investigations at this Observatory of the lines affected in sun-spots, a number of photographs in the blue and violet regions of the large sun-spot of the latter part of June were obtained, and a study of these showed the existence of a considerable number of spot lines, some of which occur as far to the violet as λ 3900. The possibility of applying these results to stellar spectra, and particularly to the case of *Arcturus*, at once suggested itself, and the comparison has proved of exceptional interest.

The material available for the study of the star was a plate obtained in July 1905 by Professor Hale and the writer in the course of some investigations on the practicability of using diffraction gratings for the photography of stellar spectra. This plate was taken in the first order of a 5-inch (12.7 cm) Rowland plane grating used in conjunction with two lenses of 5 inches aperture and 149 inches (3.78 m) focal length. The grating was set so that λ 4500 fell at about the center of the plate, and the plate itself was bent to a slight curve. At the time at which this photograph was taken the mirrors of the Snow telescope were considerably tarnished, and the exposure time was very long, amounting to about 23 hours, extended over portions of five nights. An accurate temperature control, however, resulted in a very satisfactory plate, giving an extent of spectrum

[1] *Contributions from the Solar Observatory*, No. 12.

[2] V. M. Slipher, "Observations of Standard Velocity Stars," *Astrophysical Journal*, **22**, 323, 1905.

of suitable strength and in good definition from λ 4350 to λ 4900. The linear scale of this plate is 1 mm = 4.3 t.-m., which is about two and one-half times as great as that of the more powerful spectroscopes used for determinations of radial velocity. The comparison spectrum employed was that of the Sun, three exposures on three of the intervening days having been made in all. This has proved of the greatest value in the study of the plate, since it has been possible to identify practically all of the stellar lines directly without the necessity of measurement, and at the same time the identical solar lines are available for comparison which were used in the estimation of the intensities of the sun-spot lines.

In the tables which follow, the comparison of the spectrum of *Arcturus* with that of spots for the region λ 4350 to λ 4900 is given in full. In view of the importance of sun-spot lines in stellar spectra, it has seemed best to publish a list of these lines for the violet region as well. The study of more sun-spot plates will, no doubt, result in the addition of other lines to this list, as well as in some modifications of the lines given. The intensities are in all cases referred to the intensities for the solar lines given in Rowland's table. The lower photographic resolution on the stellar plate has involved the combination of lines many of which are resolved on the spot plates, and in such cases the intensities of the lines combining to form the blends are given in full in the list of spot intensities. The abbreviation "n. c." indicates that the line is not affected.

The agreement of the results for spot and star in these tables is certainly very striking. Not only are the lines affected in spots similarly affected in the star, but the absolute intensities of the lines are remarkably close in the two cases. The conclusion seems to be unavoidable that the physical conditions existing in sun-spots and in the atmosphere of this star are nearly identical. Should it prove, as seems at present very probable, that the differences between the spectrum of the Sun and that of spots are to be accounted for on the basis of a lower temperature in the latter, we must also infer a lower temperature for *Arcturus* than for the Sun.

A study similar to this on the spectrum of *α Orionis*[1] has shown

[1] Hale and Adams, "Sun-spot Lines in the Spectra of Red Stars," *Astrophysical Journal*, **23**, 400, 1906.

λ	Element	Intensity in Sun	Intensity in Spot	Int'nsity in Star	Notes
3905.66	*Si*	12	10		
3910.98	*Fe–V*	4	5		
3913.61	*Ti*	5	4–5		
3921.56	*Ti*	1	2		
3924.67	*Ti*	4	5		
3930.02	*Ti*	2	3		
3964.32	..	1	4		
.42	*Ti*	2			
3982.63	*Ti*	2	7		
.74	*V*	3			
3984.48	*Cr*	2	3		
3991.83	..	2	3		
3996.68	*Sc*	oo	o		
3998.79	*Ti*	4	5		
4053.98	*Cr–Fe–Ti*	3	2–3		
4060.42	*Ti*	1	2		
4082.59	*Sc–Fe–Ti*	3	4		
4090.73	*V*	1	2		
4092.82	*V, Ca*	3 d?	4		
4095.09	*Ca?*	4	5		
4099.94	*V*	2	3–4		
4105.32	*V*	2	3–4		
4112.87	*Ti*	1	2–3		
4113.07	..	1	3–4		
.12	*Fe*	3			
4115.33	*V*	3	4		
4116.63	*V*	1	o		
.71	*V, Fe?*	o			
4123.54	*Cr*	o			
.66	*Ce, V–Mn*	1	3–4		
.71	*Ti*	ooo			
4147.84	*Fe*	4	5–6		
4159.35	..	5	4–5		
4186.28	*Ti*	1	2		
4190.87	*C, Co*	1Nd?	2		
4200.15	*Fe*	2	3–4		
.26	*Cr*	oo			
4209.98	*V*	1	2		
4216.35	*Fe*	3 d?	4		
4232.76	*V*	oo	3		
.89	*Fe*	2			
4252.39	..	oo	1–2		
.47	*Co*	o			
4258.48	*Fe*	2	3–4		
4283.17	*Ca*	4	5		
4295.91	*Cr, Ti*	2	3		
4299.15	*Ca*	3	4		
4299.80	*Fe, Ti*	2	3		
4300.21	*Ti*	3	2–3		
4300.73	*Ti*	2	2–3		
4302.69	*Ca*	4	5–6		
4330.19	*V*	o N	2		
4332.99	*V*	o	1–2		
33.08	..	o			
4337.72	*Cr*	3	4		

λ	Element	Intensity in Sun	Intensity in Spot	Int'nsity in Star	Notes
4338.08	*Ti*	4	3		
4338.43	*Fe*	1	1–2		
4339.62	*Cr*	4	5		
4340.63	*H*	20 N	15		Weakened on red edge mainly
4341.17	*V*	0	2		
4347.40	*Fe*	1	2		
4351.00	*Ti*	1	0		
4351.22	*Cr*	3	4		
4352.91	*Fe*	4	6–7	7–8	Widened to red
53.04	*V*	0			
4355.26	*Ca?*	2	2–3	3	
4356.06	..	0	2	2	
.16	*Ni*	0			
4363.63	..	0	1–2	2	
.77	..	0			
4367.75	*Fe*	5	6	n.c.	
.84	*Ti*	2			
4371.14	*Zr*	1	n.c.	6	
.22	..	1	n.c.		
.32	..	00	n.c.		
.44	*Cr*	2	3–4		
4372.50	..	0 d?	1	1	
4373.42	*Cr*	1	2	2	
4382.85	*Mn*	0	1	..	In star this line is covered by shading of λ 4383.72
.93	*–Fe*	2			
4387.01	*Ti?*	1	0	..	
4390.15	*V*	2	3–4	3–4	
4391.82	*Co*	0	3	5	
91.92	*Cr*	1			
92.03	*Co*	0	2		
92.24	*V?*	1 N			
4393.20	*V?*	0	1	0–1	
4395.20	*Ti*	3	3–4	7	
.41	*V, Zr*	2	3		
4400.74	*V*	1	2–3	3	
4406.81	*V–*	2	4	5	
4407.81	*V*	2	7–8	7	
.87	*Fe*	4			
4408.36	*V*	2	3	3	
4408.58	*Fe*	3	6	6	
.68	*V*	2			
4412.30	*V*	00	2–3	4	
.42	*Cr*	0			
4416.64	*V*	0	2–3	3	
4416.98	..	2	1–2	1	
4417.45	*Ti*	0	2	3	
.58	*Co*	00			
4419.94	*Mn*	00 N	1	1	
20.10	*V*	00 N			
4421.73	*V*	0	2	2	
4423.30	*Fe*	1	2	2–3	
.43	*Cr*	0 N			
4426.20	*Ti*	0 Nd?	2	2	
4427.27	*Ti*	2	3	8	
.48	*Fe*	5	n.c.		

λ	Element	Intensity in Sun	Intensity in Spot	Int'nsity in Star	Notes
4428.71	*V–Cr*	1 d?	2	2	
4429.96	*V*	∞	1	1–2	
4433.95	*Fe*	1	n.c.	2	
34.17	*Ti*	oNd?	1		
4435.13	*Ca*	5	6	8	
.32	*Fe*	2	n.c.		
4436.31	*V*	o	2	3–4	
.52	*Mn*	2	n.c.		
4437.73	..	o	n.c.	4	
37.86	..	∞	n.c.		
38.01	*V*	o	2		
4441.88	*V–*	3Nd?	5	4–5	
4443.98	*Ti*	5	4–5	4–5	
4444.57	*V–Ti*	∞	2	4	
.73	*Fe, Ti*	2	n.c.		
4445.64	*Fe*	1	2–3	2–3	
4449.31	*Ti*	2	2–3	n.c.	
4452.17	*V*	o N	2	2	
4453.88	*Ti*	1	1–2	1–2	
4455.98	*Mn*	2	6–7	6	
56.06	*Ca*	3			
4456.79	*Ca*	2	3–4	3	
4459.92	*V*	1	3	3	
4460.39	*V*	o	4	4	
.46	*Mn*	1			
.52	..	o			
4462.16	*Fe–Mn*	3Nd?	3–4	4	
4465.98	*Ti*	1	2	1–2	
4468.66	*Ti–*	5	4–5	n.c.	
4469.87	*V*	∞	o	..	Blended in star with lines to violet
4471.41	*Ti*	o	2	1–2	
4471.72	..	∞ N	1–2	2–3	
.85	..	o			
.97	..	∞			
4475.03	*Ti*	o	1–2	2	
4488.49	..	1	o–1	n.c.	Enhanced line of *Ti*
4496.12	..	1	n.c.	4	
.32	*Ti*	1	2		
4497.84	*Ti*	o N	1–2	1	
4501.44	*Ti*, –	5	4	4–5	
4503.93	..	∞	1	n.c.	
04.04	*Mn*	∞			
4508.46	*Fe?*, –	4	3	2–3	
4512.91	*Ti*	3	4–5	4	
4518.20	*Ti*	3	4–5	4	
4518.75	..	o	2	2–3	
.87	*Ti*	o			
4522.69	*Fe?*	o	n.c.	7	4522.80 is an enhanced line of *Fe*
.80	..	3	2		
.97	*Ti*	2	4		
4527.49	*Ti*	3	5	5	
.63	..	o			
4533.42	*Ti*	4	5	5	
4534.95	*Ti*	4	5	5	

λ	Element	Intensity in Sun	Intensity in Spot	Int'nsity in Star	Notes
4535·74	*Ti*	3			
.88	*Cr*	1	5–6	6	
.91	*Zr*	0			
4536.09	*Ti*	2			
.22	*Ti*	2	5–6	6	
4540.67	*Cr*	2	3	n.c.	
4544·79	*Cr*	1			
.86	*Ti*	3	5	5	
4545·51	*Cr–V*	0	1	1	
4546.13	*Cr*	3	4	4	
4548·94	*Ti*	2	3	3–4	
4549·64	*Fe*	2			
.81	*Ti–Co*	6d?	7	6	
4552.63	*Ti*	2			
.72	*Fe*	1	4–5	4	
4555.66	*Ti*	3	4–5	4	
4556.06	..	3	2		
.31	*Fe–Cr*	4	n.c.	5	
4558.83	*Cr?*	3	2	1	Enhanced line of *Cr*
4560.10	*Ni, Ti*	0	1	2	
4562.81	*Ti*	00	1–2	2	
4563.94	*Ti*	4	3–4	3	
4569.69	*Cr*	00	1–2	1–2	
.79	*Cr*	0			
4571.28	*Mg*	5	6	7	
4571.85	*Cr*	1	1–2	1–2	
4572.16	*Ti–*	6	5	4–5	
4574.90	*Fe*	2			
75.08	..	00 Nd?	3	3–4	Widened to red
4575·73	*Zr*	00 N	0–1	1	
4576.51	..	2	1	1	
4577·36	*V*	0	2–3	3	
4578.73	*Ca*	3			
.91	*V*	00 N	5	5	
4580.23	*Cr*	3	4–5	4–5	
4580.59	*V*	1	2–3	3	
4581.58	*Ca*	4			
.69	*Co, Fe*	4	10	10	
4584.02	*Fe–*	4	3	3	Enhanced line of *Fe*
4586.05	*Ca*	4			
.16	..	0	6	5–6	
4586.55	*V*	1	3	3–4	
4588.38	..	3	2	1	Enhanced line of *Cr*
4594.30	*V*	2 N	4–5	4	
4600.93	*Cr*	3	5		
01.11	..	0	n.c.	6	
01.21	*Cr*	0	0–1		
4603.13	*Fe*	6	7–8	7	
4606.40	*Ni, C*	2	3	2–3	
4607.51	*Sr*	1	2–3	2	
4616.30	*Cr*	4	6	5	
4617.45	*Ti*	3	4–5	4	
4619.71	*Cr*	1	1–2		
.96	..	00	1–2	3–4	
4620.69	*Fe*	1	0	0	

λ	Element	Intensity in Sun	Intensity in Spot	Int'nsity in Star	Notes
4622.06	*Cr*	0	3	3	
.13	*Cr*	1			
4623.28	*Ti*	2	3	3	
4626.36	*Cr*	5	7	6	
4630.31	*Fe*	4	5	5	
4635.35	*V*	∞ N	1–2	1–2	
4639.54	*Ti*	2	4	4–5	
.68	*Cr*	0			
4639.85	*Ti*	2	3–4	7	
40.12	*Ti*	1	3–4		
4645.37	*Ti*	0	2	2–3	
4646.35	*Cr*	5	6	6	
4650.19	*Ti*	0	1	1–2	
4651.46	*Cr*	4	6	5	
4652.34	*Cr*	5	7	7	
4653.55	..	∞	1–2	1	
.68	..	∞			
4656.23	*Ti*	0	1–2	1–2	
.36	*Cr*	0			
4656.64	*Ti*	3	5	5	
4657.38	*Ti?*	2	1	1	
4664.96	*Cr*	3	4	n.c.	
4668.75	..	1 N	2–3	2	
4670.59	..	2	3	4	
4675.29	*Ti*	1 N	2	2	
4680.48	..	1	2	2	
4682.09	*Ti*	3	5	5	
4685.45	*Ca*	2 N	3	3	
4687.85	..	∞	1–2	2	
.98	*Zr*	0			
5688.36	*Fe*	2	1	2–3	
.55	..	0	1		
4690.98	*Ti*	∞	0–1	1	
4693.85	*Ti*	0	1–2	2	
4698.58	*Co*	0	n.c.	5	
.64	*Cr*	1	n.c.		
.80	*Cr*	1	n.c.		
.95	*Ti*	1	2		
4710.37	*Ti*	∞	5	5	
.47	*Fe*	3			
4715.47	*C?*	∞	2	2–3	
4717.76	..	0	1	2	
4718.60	*Cr*	3	4	n.c.	
4722.80	*Ti*	0	2	2–3	
4723.29	*Cr*	∞	3	4	
.36	*Ti*	∞			
4729.86	*Fe? Cr*	1	1–2	1–2	
4733.78	*Fe*	4	6	6	
4742.98	*Ti*	1	2	2	
4744.01	..	∞∞	1	..	
4744.57	*Fe?*	3	2	2	
4748.32	*Fe?*	4	3	2	
4752.01	*Na?*	∞	0–1	0	
4755.34	..	∞	0	..	
4756.30	*Cr*	2	3–4	3	

λ	Element	Intensity in Sun	Intensity in Spot	Int'nsity in Star	Notes
4758.31	*Ti*	1	2	2	
4762.57	*Mn*	5	6	7	
4771.28	*Ti–Co*	00	1	2	
4778.44	*Ti*	00	0–1	0	
4779.63	*Fe*	1	2	2	
4781.91	..	00	1–2	2–3	
4789.53	*Cr*	2	3	3	
4792.70	*Ti–Cr*	2	3	3–4	
4799.98	*Ti*	1	2	2	
4805.61	*Ti*	0	1	2	
4807.18	*Ni*	2	1–2	1–2	
4820.59	*Ti*	1	3	3	
4821.31	..	0	000	00	
4823.70	*Mn*	5	6–7	6	
4825.53	..	00	1	1	
.67	*Ti*	000			
4827.64	*V*	000	2	2–3	
.80	*Ti*	00			
4829.55	*Cr*	2	3	3	
4831.36	*Ni*	3	2–3	2	
4831.83	*V*	00	2–3	3	
4832.62	*V*	00	2	3	
4832.90	*Fe*	3	2	2	
4836.42	..	0	00	00	
4841.07	*Ti*	3	4–5	4	
4847.50	*Ca*	0	2	1–2	
4848.44	..	2	n.c.	3	
.60	*Ti*	0000	0–1		
4849.08	*Fe*	1	1–2	1–2	
4851.69	*Ca, V*	1	3–4	4–5	
4856.20	*Ti*	1	3	3	
4861.53	*H*	30	25	25	
4862.03	*Cr*	0	2	..	In star this line is lost in shade of *Hβ*
4864.92	*V*	0	3	3	
4868.45	*Ti*	0	1–2	3	
.60	..	00 d?	n.c.		
4870.32	*Ti*	1	2	2	
4875.67	*V*	1	3	3	
4876.59	..	1	0	0	
4881.74	*V*	1 N	3	5	
.90	*Fe*	2	n.c.		
4885.26	*Ti*	2	3–4	3	
4885.96	*Cr*	0	1–2	n.c.	
86.13	*Cr*	00			
4888.71	*Cr*	00	4	3–4	
.82	*Fe*	2			
4893.03	*Fe*	1	0–1	0	
4900.10	*Ti, La*	2	3–4	4	

that sun-spot lines are also present in the spectrum of that star. The amount by which they are affected, however, is, as a rule, considerably greater than in the case of spots or of *Arcturus*. We have, accordingly, in Sun, *Arcturus*, and *α Orionis*, a series arranged in

the order of increasing differences for the characteristic spot lines. In the event referred to above—namely, that these differences can be accounted for on a temperature basis—this sequence would represent a scale of descending temperatures.

In a recent letter to Professor Hale received while this investigation was in progress, Mr. Baxandall, of the Solar Physics Observatory at South Kensington, refers to some studies of the spectrum of *Arcturus* made by himself in the blue region of the spectrum. The absence of a list of sun-spot lines in this region prevented him from making a direct comparison, but his conclusion, that most of the titanium and vanadium lines in the spectrum of *Arcturus* are considerably stronger than in the Sun, is in agreement with the results found in this discussion.

I am indebted to Messrs. Gale and Ellerman for the sun-spot plates used in this investigation.

SOLAR OBSERVATORY, MOUNT WILSON,
August 1906.

RESULTS OF SOLAR OBSERVATIONS AT PRINCETON, 1905–1906

By WALTER M. MITCHELL

The preliminary account of the observations of reversed lines in the spectra of sun-spots at Princeton was published in this *Journal* for June 1904. A more detailed account of the observations of the sun-spot spectrum appearing about a year later, in the *Astrophysical Journal* for July 1905, gave a complete table of the wave-lengths recorded. It had been found, in looking over unpublished observations of Professor Young, that some eighteen of these reversed lines had already been observed by him during the early summer of 1892, while working with the same instrument.

Observations have been continued during the period from October 1905 to May 1906; the whole region of the spectrum F–*a* (λλ 4861–7160) has been gone over some twelve times since the observations were begun in March 1904. All observations have been made in the same manner and with the same instrument.

In comparing the results of the observations made since October 1905 with those previous to that date, it was found that the selection of widened lines in the two periods was so similar that it would not be necessary to publish these lines a second time. But this is not the case with the reversed and weakened lines, many new ones of both these classes, particularly the latter, having been observed. The table at the end of this paper gives only the reversed and the weakened lines; widened and intensified lines will be found in the table published last year.[1]

During the more recent observations of the sun-spot spectrum it has been noticed that the number of weakened lines recorded has greatly increased. Many lines that were formerly reversed were now found weakened; also many new weakened lines were found, the lines not being affected in previous observations. This change may be an indication of alteration in the general constitution of a sun-spot in connection with the passing of the sun-spot maximum,

[1] *Astrophysical Journal*, **22**, 11, 1905.

but the period of observation is too short for any definite conclusion to be drawn. Scattered light in our atmosphere often causes the

FIG. 1

FIG. 2

FIG 3

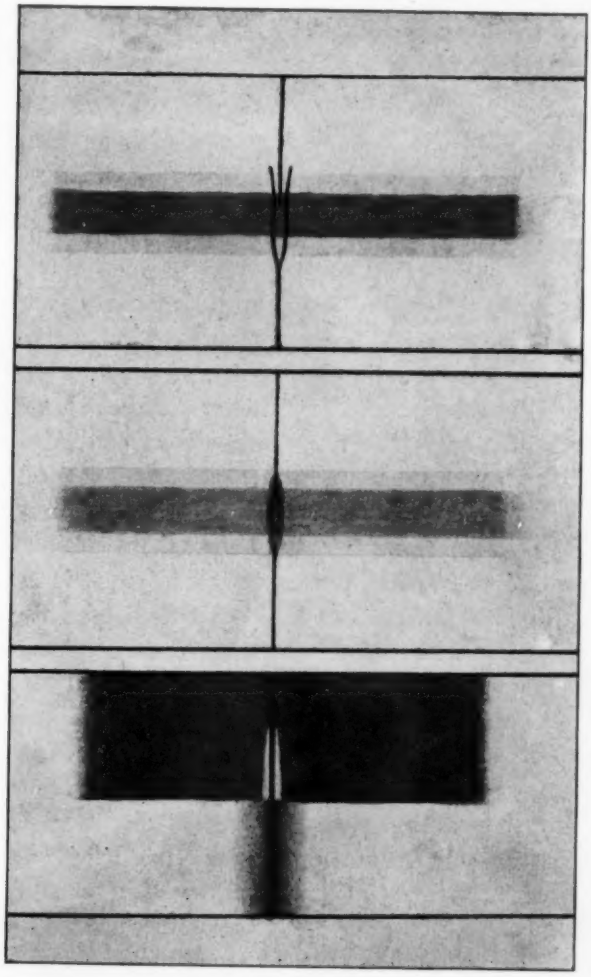


FIG. 1.— Appearance of reversed lines on Oct. 31, 1905
FIG. 2.— Weakened lines on April 3, 1906.
FIG. 3.— *b* lines in chromosphere.

reversed lines to be very indistinct, and it is probable that in several cases the indistinct reversed line has been mistaken for a weakened line. These cases are indicated in the table. It has been observed

that generally the more reversals there are in the spectrum of a spot, the fewer are the weakened lines and vice versa.

The existence of "veils" across the spot umbra may also cause the reversals to be less distinct. This would seem to be the case in one instance recorded on May 11, 1906. My notebook states:

> Noticed that the *Fe* lines λ5250.39 and λ5712.36 are *not* reversed where on last observation, three days ago, they were reversed strongly. Also other lines in the red are not so widely reversed as on previous date. . . . . Spot has become overgrown with veils, bridges, etc. Many red reversed lines show the weakened appearance and have dark lines partly through the weakened part.

Unfortunately, the sky clouded over very soon after observations were begun, so that other lines could not be examined in detail.

There have been several instances, in addition to the one just mentioned, in which the reversals presented a very peculiar appearance. A notable one occurred on October 31, 1905, in a large spot of the minimum type. The reversal extended considerably below the spot umbra and penumbra, while above was the very curious tripling of the spectrum line, the two halves of the reversal diverging and extending slightly beyond the penumbra, the ordinary absorption line continuing into the umbra spectrum and ending abruptly (Fig. 1). This appearance was not confined to one line, but was distinctly seen in all the more widely reversed *Fe* lines and one *Ni* line, in various parts of the spectrum. Several instances were recorded where the reversed part of the line was displaced slightly to one side, instead of being central. Another curious case was recorded on April 3, 1906, where on one side of the spot the lines were distinctly reversed, while on the other side the same lines were weakened, with a continuation of the dark line extending into the weakened part (Fig. 2). This was observed in all the reversed lines on that date. The probable cause of these curious weakened lines seems to be condensation of the gases of the spot, forming a thin photosphere over portions of the penumbra and umbra in the shape of veils. The thin photosphere, making a brighter background than the dark spot umbra, tends to bring out the ordinary absorption line.

With the more widely reversed lines it was found possible to measure the distance between the two components. The mean distance between the components of the various reversed lines thus measured

was 0.189 t.-m. The probable error of the mean of five measures of the width of the reversed line λ 6173.55 was found to be 0.0077 t.-m. The detailed results of the measures are given in the table.

It was thought that possibly the gas masses causing the reversed lines (of iron) might be similar to the iron flocculi photographed by Hale and Adams at Mount Wilson,[1] but careful examinations of the whole disk have so far failed to reveal reversals anywhere but over the spot umbra and occasionally in the immediate vicinity of the spot. Hence it seems safe to say that the reversals of such lines as I have recorded exist only in the regions mentioned, indicating most probably that the gases causing them are essentially different from the flocculi, since these are well distributed over the whole disk.

If a curve is drawn the ordinates of which are the percentage of lines reversed to total number affected in a given region, while the abscissæ are the wave-lengths of these regions, it will be found that there is a very decided maximum at λ 6200. From Wien's law, $\lambda T = \text{const.}$, we find 4700° for the temperature of the gases producing the reversed lines (using 2940 for the constant, the value found by Lummer for a black body). Adopting 6000° as the photospheric temperature, we find from Stephan's law the value 0.38 for the ratio of sun-spot radiation to photosphere radiation, a value in very close agreement with 0.41 deduced by Wilson from direct observation.[2]

Observations of the band-lines have been made whenever possible. On three occasions they have been observed below B extending to approximately λ 7100. The regions in which I have found that they are seen are:

λλ 7100–6760. From λλ 6760–6450 the spectrum is only occasionally resolved and then generally indistinct and blurred.

λλ 6450–6360. In this region I remarked[3] that the fine lines of the spot spectrum were arranged into groups. Several of the large spots visible in the fall of 1905 showed that two of these groups had the appearance of short flutings, the wave-lengths being λ 6389

[1] *Astrophysical Journal*, **23**, 62, 1906.

[2] *Monthly Notices*, **55**, 461, 1895.

[3] *Astrophysical Journal*, **19**, 359, 1904.

and λ 6381. Fowler also records[1] two "well-developed flutings" at these wave-lengths. From λλ 6360–5700 the band-lines are generally faint and indistinct.

λλ 5700–5200. In this region they become fairly prominent.

λλ 5200–5000. The band-lines here are very conspicuous.

Hence it can be said that the resolution of the spot spectrum into fine lines is least likely to be seen in the neighborhood of C and the D lines, while above λ 5000 they have as yet not been observed. In the vicinity of B the appearance is similar to that in other regions. As visual observations are not well adapted for the purpose, I have made no attempt to determine the wave-lengths of these lines.

THE CHROMOSPHERIC SPECTRUM

It has been found that generally the visibility of the chromospheric lines depends more upon the state of the Earth's atmosphere—i. e., the "seeing"—than on the state of the chromosphere. Many lines have been seen when the slit was set on parts of the chromosphere that were absolutely without prominences or eruptions of any kind. It thus seems that an eruption or prominence is not essentially necessary to render the chromospheric lines visible; a sufficiently large solar image and steady seeing should render the majority visible whether there is a chromospheric disturbance or not. It was frequently noticed during the moments of good seeing that many lines flashed out, only to disappear again with the return of atmospheric unsteadiness.

Several lines have been found to be always doubly reversed. The most prominent of these are the *b* lines. b_1, b_2, the lower (enhanced iron) component of b_3, are usually quite bright, while the upper (magnesium) component of b_4 is fainter and more difficult to see. The appearance of b_1 and b_2 in the chromosphere gives one the impression that the usual dark wings have been replaced by narrow bright ones, the central dark absorption line retaining its usual width and darkness, the reversals being, as one might say, outside the absorption line (Fig. 3). b_3 and b_4 are reproductions on a smaller scale, and are best seen with a very high dispersion fourth-order spectrum of a 20,000 line grating.

One very notable instance of chromospheric activity was recorded

[1] *Monthly Notices*, **65**, 217, 1905.

on May 13, 1906, at $8^h\ 15^m$ G. M. T. One of a pair of medium-sized spots was just going off the limb, the other being inside of it and nearer the Sun's equator. A very hasty examination showed that practically every dark line, as nearly as could be estimated, was bright over the region of the departing sun-spot. Owing to the short duration of the outburst, about 25 minutes, it was possible to record only a few of these bright lines. Out of a total of 83 lines recorded 62 were doubly reversed, the appearance being similar to that of the *b*'s described above. The majority of these doubly reversed lines were heavy iron lines which are winged in the spot spectrum. The usual chromospheric lines (those in Young's list with a fairly high frequency) were in the majority of instances *not* doubly reversed, but simply much brighter than under ordinary circumstances. When the slit was set making a small angle of 5° or 10° with the Sun's limb, which position I have found best for chromospheric observation, it was seen that the bright chromospheric lines made a small angle toward the red with the ordinary Fraunhofer line, apparently indicating that with increasing distance from the Sun's center the chromospheric gases were receding with increasing velocity.

By a suitable adjustment of the spectroscope the chromospheric spectrum was obtained simultaneously with that of the remaining sun-spot: the difference between the two spectra was most striking and showed clearly the effects of the widely differing physical conditions in the chromosphere and the spot. From the great difference between the two classes of chromospheric lines it seemed as if there were different forces at work producing them. The doubly reversed lines might perhaps be the result of anomalous dispersion, as has been suggested by Julius.[1]

In a recent paper[2] Fowler calls attention to the fact that the enhanced lines of iron, titanium, and chromium appear as high-level lines in the chromosphere, while in the spot spectrum the corresponding Fraunhofer lines are enfeebled or weakened. My own observations agree in the main with Fowler's. However, the enhanced *Ti* line at λ 5154.24 has not been seen, nor is it given in Young's revised list. Some investigations which I made during

[1] *Astrophysical Journal*, **15**, 28, 1902.

[2] *Monthly Notices*, **61**, 361, 1906.

the last winter on the spark spectrum of iron and titanium confirm the results given by Fowler, with the addition that the line λ 6247.77 is probably an enhanced line of iron.

The question arises what may be the possible explanation of the prevalence of enhanced lines in the chromospheric spectrum. Lockyer has attempted to explain this on the supposition that the temperature of the chromosphere is that of the electric spark.[1] In an analogous manner, Scheiner[2] suggested that the temperature of certain stars might be determined by presence of certain spark lines in their spectra, the *Mg* line λ 4482 in particular. But Hartmann and Eberhard have shown[3] that these conclusions are unjustifiable, and since an atmosphere of hydrogen will produce the spark lines in the arc spectrum, they suggest that the prominence of λ 4482 is due to the abundance of hydrogen in the atmospheres of the stars of the particular type. It therefore seems possible that the prevalence of hydrogen in the chromosphere may cause certain lines to be suppressed, at least to such an extent that they become invisible against the background of the sky spectrum. This would be borne out by the observations of Fowler mentioned above, for he states that the high-level lines are enhanced lines, as would be supposed, since it is probable that high in the chromosphere the proportion of hydrogen is greatest, while low in the reversing layer, where the proportion of hydrogen is probably much less, other lines beside those found in the spark spectrum make their appearance. The emission coefficient of these high-level lines being greater than that of the lines caused by lower-level gases, the absorption of the lines would not be so great, hence across the dark umbra of the spot the line would have an enfeebled or weakened appearance.

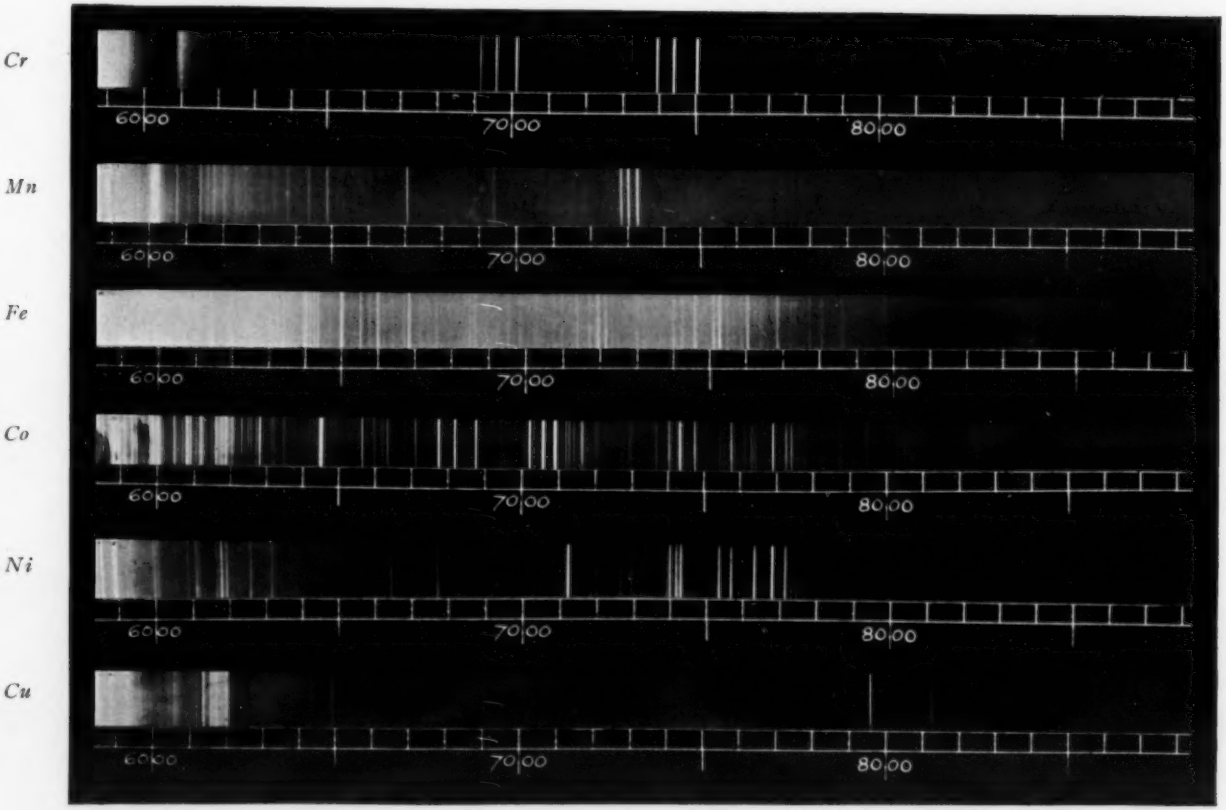
But these views cannot be fully confirmed until additional investigations have been made of arc spectra in hydrogen, since up to this time investigators have confined themselves to the violet regions of the spectrum alone. Nevertheless it seems probable, should the investigations be extended to the longer wave-lengths, that a state of affairs will be found altogether similar to that found in the more refrangible regions.

[1] *Proc. R. S.*, **68**, 178, 1901.

[2] *Astronomy and Astro-Physics*, **13**, 569, 1903.

[3] *Astronomische Nachrichten*, **161**, 314, 1903.

PLATE III



PHOTOGRAPHS OF ARC SPECTRA

TABLE I

Wave-Length	Element	Spot Spectrum					Chromosphere		Remarks
		Total No. Obs.	Reversed		Weakened				
			No. Obs.	Inten.	No. Obs.	Inten.	No. Obs.	Inten.	
4876.59		1			1	−5			
4918.19	*Fe*	1			1	−1			Hazy.
4921.96	*La–Ti*	7					3	7	Always darkened in spot.
4924.11	p*Fe*						3	15	Double reversal twice in chromosphere.
4925.75	*Ni*	2			2	−1			
4934.4	*Ba?*						3	5	Double reversal once, w.-l. seems to be somewhat longer than that of *Ba* line.
4952.46	*Fe*	2			1	−1			
4952.82	*Fe*	4			2	−2			
4953.39	*Ni*	2			1	−1			
4970.09	*Fe*	3			2	−1			Generally hazy.
4993.53							1	5	
4998.41	*Ni*	2			2	−3			Obliterated once.
4999.69	*Ti–La*	2			2	−2			
5015.80	*He*						3	7	Probably a high level line.
5018.63	p*Fe*						3	10	Double reversal twice. The red component.
5027.94	*Fe*	4			2	−4			
5039.54	*Ni*	6			3	−4			Generally weakened and hazy.
5061.70		1	1	10					
5061.88		1	1	10					
5072.85	*Fe*	1			1	−4			
5080.71	*Ni*	4			4	−3			
5081.29	*Ni*	1			1	−2			
5082.53	*Ni*	7			7	−4			Obliterated twice, other times weakened.
5087.60	*Y*						1	10	
5112.46							2	5	Wave-length longer than given by Young.
5114.43							1	2	
5120.59	*Ti*	6			2	−2	1	2	
5123.39	*Y*						2	3	
5129.81	*Fe*	6			6	−4			Obliterated four times.
5130.54	*Ni*						1	2	Probably high level.
5131.64	*Fe*	2	1	5	1	−3			Hazy both times.
5145.27	*Fe*	6			1	−2			Generally widened and hazy in spot spectrum.
5159.23	*Fe*	1			1	−4			
5164.72	*Fe?*	1			1	−3			
5165.42	*C*						1	1	Very faint.
5165.59	*Fe*	5			4	−3			
5167.50	*Mg*						5	10	The upper component of b_4 generally doubly reversed.
5168.83	*Ni*	2			2	−2			
5169.22	p*Fe*	7			7	−3	5	25	The lower component of b_3, always doubly reversed in chromosphere; weakened in spot.
5170.94	*Fe*	2			2	−3			
5171.78	*Fe*	1			1	−5			
5172.86	*Mg*						5	30	b_2. Always double reversal.
5173.92	*Ti*						1	1	
5183.79	*Mg*						5	30	b_1. Always double reversal.
5186.07	p*Ti*	2			2	−3			
5187.80							1	5	Is not the *Fe* line λ 5188.08.

TABLE I—*Continued*

Wave-Length	Element	Spot Spectrum					Chromosphere		Remarks
		Total No. Obs.	Reversed		Weakened				
			No. Obs.	Inten.	No. Obs.	Inten.	No. Obs.	Inten.	
5188.08	*Fe*	2			2	−2			
5189.0	*Ti–Ca*						4	5	Not sure which component reverses. Fowler gives origin of λ 5188.86 as p *Ti*.
5191.63	*Fe*	2	1	?					
5196 23	*Fe*	6			5	−3			
5197.74	p*Fe*	2			1	−4	5	15	High level line, double reversal once.
5200.36	*Cr*						1	5	
5202.52	*Fe*	4			1	−1	1	7	Double reversal in chromosphere.
5204.70	*Cr–Fe*	5			2	−1	1	10	Double reversal in chromosphere.
5205.90	*Y*	1			1	−4	2	3	
5206.22	*Cr–Ti*	5			2	−2	2	9	Double reversal in chromosphere. Generally winged in spot.
5208.78	*Fe*						1	10	Double reversal in chromosphere.
5225.70	*Fe*	6	5	4					
5225.97	*Cr*	4	3	3					
5226.71	p*Ti*	2	1	?	1	−4	3	6	
5227.04	*Fe–Cr*	8	3	2	3	−3	1	4	Double reversal in chromosphere.
5227.36	*Fe*	1			1	−1	1	4	Double reversal in chromosphere.
5234.79	p*Fe*	2			2	−3	5	15	High level line. Double reversal
5237.49	p*Cr*	4			4	−3	1	5	once.
5239.99		1			1	−3	2	5	
5247.23	*Fe*	5	4	2					
5247.74	*Cr*	8	6	3					Young's chromosphere line.
5249.8							2	2	
5250.39	*Fe*	12	9	10					Frequently reversed outside of spot umbra, width of reversal 0.170 t.–m.
3253.63	*Fe*	1	1	1					
5255.30	*Cr*	5	2	2					
5255.8							2	1	Not sure of this line.
5260.0							2	2	
5260.56	*Ca*	11	4	5					Young's chromosphere line.
5264.98							1	7	
5269.72	*Fe*						3	7	E_2, Double reversal twice.
5270.50	*Ca–Fe*						2	5	E_1, Double reversal once. Not sure which component.
5273.34	*Fe*						2	4	Double reversal once.
5274.58							2	2	
5275.93	*Cr*	10	5	5					
5276.17	p*Fe*						5	8	Not sure of wave-length.
5284.28	*Ti*	1			1	−5	5	6	
5284.79		2			1	−4			
5293.21	Awv?						1	5	
5298.19	*Cr*	4	1	2	1	−2			
5298.46	*Cr*	4	1	?	1	−2			
5298.67	*Ti*	5	2	2	1	−2			
5298.96	*Fe*	2	1	1	1	−3			
5300.93	*Cr*	7	2	3					
5304.36	*Cr*	6	1	2					

TABLE I—*Continued*

Wave-Length	Element	Spot Spectrum					Chromosphere		Remarks
		Total No. Obs.	Reversed		Weakened				
			No. Obs.	Inten.	No. Obs.	Inten.	No. Obs.	Inten.	
5306.04							1	5	
5307.54	*Fe*						1	4	Double reversal.
5308.60							1	5	
5313.03	*Cr*	2	1	2					
5316.79	p*Fe*						5	20	Double reversal twice.
5320.0?	*Fe*						2	7	Not sure of wave-length.
5321.0?							1	2	Not sure of wave-length.
5324.37	*Fe*						1	3	Double reversal. Winged in spot.
5325.74							2	10	Wave-length seems to be greater than that given by Young. One observation by Young records "disappears in spot spectrum."
5328.24	*Fe*						1	15	Winged in spot. Double reversal in chromosphere.
5328.75	*Fe*						1	10	Double reversal.
5329.33	*Cr*	4	1	1			1	4	Double reversal.
5329.97	*Cr*	7	1	?	1	−4			
5330.18	*Fe*						1	4	Double reversal.
5335.05	*Co*						1	5	
5336.97	p*Ti*						1	20	Double reversal.
5337.91	"						1	5	
5340.12	*Fe*	1			1	−2	1	3	Double reversal.
5341.21	*Fe*						1	3	Double reversal.
5345.99	*Cr*	4			2	−2			Thinned and winged.
5348.51	*Cr*	5			2	−2			Thinned and winged.
5349.93	*Fe*	2	1	?	1	−2			
5353.70	*Co*						2	4	Double reversal.
5361.81		2			1	−2	3	5	Double reversal.
5363.06	p*Fe*						3	8	
5365.07	*Fe*						1	3	Double reversal.
5365.60	*Fe*						1	3	Double reversal.
5367.67	*Fe*						1	3	Double reversal.
5370.17	*Fe*						1	2	Double reversal.
5371.66	*Cr?*						1	10	Double reversal.
5373.91	*Fe,Cr*	5	1	?	3	−3			
5377.80	*Mn*	2			2	−4			
5379.77	*Fe*						1	10	Double reversal.
5381.22	*Fe*						1	3	Double reversal. There is a p*Ti* line at λ 5381.204. This may be it and not the *Fe* line.
5382.47		1			1	−3			
5389.68	*Fe*						1	3	Double reversal.
5394.85	*Mn*	11	2	2					Generally widened and darkened.
5399.67	*Mn*	6	3	5					
5401.47		4	1	?	3	−4			Bright over spot on one occasion.
5405.99	*Fe*						1	3	Double reversal.

TABLE I—*Continued*

Wave-Length	Element	Spot Spectrum					Chromosphere		Remarks
		Total No. Obs.	Reversed		Weakened				
			No. Obs.	Inten.	No. Obs.	Inten.	No. Obs.	Inten.	
5409.34	*Fe*	2	1	2	1	−2			
5410.00	*Cr*						1	5	
5411.12	*Fe*						1	4	Double reversal.
5413.89	*Mn*						1	10	Hazy in spot.
5415.42	*Fe–V*						1	4	Double reversal.
5418.98	*Ti?*						1	3	Double reversal.
5425.46		3			3	−3	2	7	Young observes "very much weakened in spot."
5429.91	*Fe*						1	2	Double reversal.
5432.75	*Mn*	11	3	7					Generally much widened and darkened.
5433.16	*Fe*						1	5	Double reversal.
5434.74	*Fe*						1	10	Double reversal. Winged in spot.
5436.51	*Fe*	6	1	2	3	−2			
5436.80	*Fe*	9	4	5	2	−2			
5445.26	*Fe*	3			2	−2	1	5	Double reversal. Thinned in spot.
5447.13	*Fe*						1	3	Double reversal.
5455.83	*Fe*						1	3	Double reversal.
5460.72		12	1	?					Always strongly darkened.
5461.76		9	7	6					
5462.71	*Ni*	8	7	7	1	−2			Weakened observation may be mistake for reversal.
5467.20	*Fe*	4	1	?	1	−2			
5470.84	*Mn*	10	2	10					
5483.31	*Fe*	5	4	3	1	−2			Weakened observation may be mistake for reversal.
5493.71	*Fe*	3	2	4	1	−3			
5494.68	*Fe*	5	3	4	1	−1			
5495.10	*Ni*	4	4	9					
5497.74	*Fe*	9	1	?			1	4	Double reversal. Winged in spot.
5501.68	*Fe*	5					1	5	Double reversal. Winged in spot
5506.10	*Mn*	8	1	5					
5511.87	*Fe*	1	1	8					
5527.03	*Si*						2	10	Double reversal once. Fowler gives origin as p*Sc*.
5528.64	*Mg*	3					1	10	Winged in spot.
5535.06	*Fe*	1			1	−3	4	12	Fowler gives origin as p*Fe?*
5537.97	*Mn*	11	5	10					
5538.74	*Fe*	10	8	9	1	−2			
5544.16	*Fe*	3	2	1					
5546.73	*Fe*	6	2	4	1	−3			
5569.85	*Fe*						1	4	Double reversal.
5573.07	*Fe*	2					1	3	Double reversal. Winged in spot.
5576.32	*Fe*						1	4	Double reversal.
5584.53	*V*	7	1	6					
5586.99	*Fe*	3					1	3	Double reversal. Winged in spot.
5588.98	*Ca*	4					1	3	Winged in spot.

TABLE I—*Continued*

Wave-Length	Element	Spot Spectrum					Chromosphere		Remarks
			Reversed		Weakened				
		Total No. Obs.	No. Obs.	Inten.	No. Obs.	Inten.	No. Obs.	Inten.	
5594.69	*Ca*						1	3	Not sure which component reverses.
5594.88	*Fe*	2			2	−3			
5615.88	*Fe*						1	3	Double reversal.
5619.82		6	2	2	1	−3			
5620.72	*Fe*	5	2	?	3	−4			
5625.54	*Ni*	1			1	−4			
5627.9							1	2	Do not think that this is the *V* line.
5636.93	*Fe*	2	1	4					
5637.63	*Fe*	2	1	4					
5641.21		3	2	5	1	−3			
5645.83	*Si*	3			3	−4			Obliterated once.
5648.00							1	4	Wave-length uncertain.
5654.09	*Fe*	2	1	2					
5657.66	*V*	11	1	6			1	8	Reversed? twice in spot.
5658.10	*Y*,–	4	4	3					
5663.16	*Ti-Fe-Y*	7					1	10	Widened and darkened in spot.
5667.37		2	1	10					
5667.74	*Fe*	2	1	9					
5668.59	*V*	11	2	6					
5669.26	*Sc?*	3	1	1	2	−3			
5684.71	*Si*	4			4	−3			
5690.65	*Si*	5			5	−3			
5701.32	*Si*	2			2	−3			
5708.62	*Si*	3			3	−2			Obliterated once.
5712.36	*Fe*	8	8	7					
5722.10							1	1	Very faint.
5727.87	*Cr?*	10	1	8					
5731.44	*V*	10	1	9					Reversed? four times.
5731.98	*Fe*	1			1	−2			
5739.87		8	1	6					
5742.07	*Fe*	1	1	3					
5746.64	A,–	2							Reversed? twice.
5748.17	*Fe*	5	1	6					Reversed? once.
5748.57	*Ni*	8	6	4					
5781.13	*Cr–Ti*	5	3	2					
5781.40	*Cr*	8	8	8					
5781.97	*Cr*	8	8	10					Width of reversal 0.197 t.-m.
5783.29	*Cr*	7	7	5					
5784.08	*Cr*	7	6	3					
5784.88	*Fe*	6	6	4					
5785.19	*Cr*	7	6	5					
5785.50	*Fe*	6	4	4					
5786.19	*Ti Cr*	6	2	2					
5798.08		7	1	?	2	−3			
5847.22	*Ni*	5	1	?					
5853.90	*Ba?*						1	5	

TABLE I—*Continued*

Wave-Length	Element	Spot Spectrum					Chromosphere		Remarks
		Total No. Obs.	Reversed		Weakened				
			No. Obs.	Inten.	No. Obs.	Inten.	No. Obs.	Inten.	
5873.44		2	1	8					
5875.92	*He*						...	90	
5880.49		10	10	10					
5890.19	*Na*	5			1	−1	5	10	Generally doubly reversed in chromosphere.
5896.36	*Na*	5			1	−1	5	10	Generally doubly reversed in chromosphere.
5902.69	*Fe*	1	1	8					
5910.20	*Fe*	5	5	6					
5916.47	*Fe*	5	3	2					
5918.77	*Ti*	6	2	3					
5938.04		11	5	5					
5958.46	*Fe*	1	1	8					
5999.92	*Ti*	9	2	2					
6002.97		5	2	4					
6005.77	*Fe*	9	9	5					
6008.19	*Fe*	11	11	6					
6008.79	*Fe*	1	1	2					
6012.45	*Ni*	9	9	6					
6013.72	*Mn*	11	8	4					
6016.86	*Mn*	11	8	4					
6022.02	*Mn*	6	1	?					
6039.95	*V*	10	6	3					
6053.91	*Ni*	3	1	5					
6064.85	*Ti*	10	10	9					Width of reversal 0.148 t.-m.
6079.23	*Fe*	11	11	8					
6081.67	*V*	10	6	8					
6082.93	*Fe*	12	12	8					
6085.47	*Ti–Fe*	9	2	4					
6089.79	*Fe*	7	4	3					
6090.43	*Ti-V*	11	3	6					
6091.40	*Ti*	8	2	3					
6093.03	*Ti?*	9	4	6					
6093.37	*Mn?*	8	2	3					
6096.88	*Fe*	4	3	3					
6098.46		3	2	2					
6102.39	*Fe*	2			2	−3			Young's chromosphere line.
6102.94	*Ca*	11	6	4					Young's chromosphere line.
6103.40	*Fe*	3			1	−4			Young's chromosphere line.
6111.29	*Ni*	3			2	−4			Obliterated once.
6111.87	*V*	11	3	4					
6122.43	*Ca*	8	1	2					Generally much winged. Young's chromosphere line.
6125.24		2			2	−5			Obliterated twice.
6126.44	*Ti*	10	3	3					
6127.85		5	2	7					
6129.19	*Ni*	11	4	3					

TABLE I—*Continued*

Wave-length	Element	Spot Spectrum					Chromosphere		Remarks
		Total No. Obs.	Reversed		Weakened				
			No. Obs.	Inten.	No. Obs.	Inten.	No. Obs.	Inten.	
6131.79		1	1	3					
6132.07		1	1	4					
6137.21	*Fe*	12	12	10					Width of reversal 0.189 t.-m.
6141.93	*Ba–Fe*						1	5	
6142.70		2			2	−4			
6145.23		1			1	−3			
6149.46		3			3	−4			Obliterated twice. Young's chromosphere line.
6150.36	*V*	11	1	5					
6151.83	*Fe*	9	9	7					Frequently reversed outside of spot umbra.
6154.44	*Na*	11	6	6					Young's chromosphere line.
6156.24		4	2	7					
6163.97	*Ca*	8	2	?					
6170.73	*Fe–Ni*	2	2	4					
6173.55	*Fe*	12	12	10					Frequently reversed outside of spot. Average width of reversal, 0.210 t.–m. Young's chromosphere line.
6188.21	*Fe*	7	6	7					
6191.39	*Ni*	11	7	5					
6199.38	*V*	12	3	7					
6200.53	*Fe*	6	3	2					Young's chromosphere line.
6204.83	*Ni*	2	1	4	1	−3			
6210.90		10	1	4					
6213.64	*Fe*	11	11	8					
6214.08	*V*	11	3	7					
6216.57	*V*	10	5	8					Young's chromosphere line.
6219.49	*Fe*	8	1	4					Young's chromosphere line.
6224.71	*V*	11	3	7					
6226.95	*Fe*	4	3	1					
6232.86	*Fe*	11	11	9					Young's chromosphere line.
6233.08		8	3	7					Apparently no dark line at this point.
6237.53		3			3	−3			
6238.60		5			5	−4			Young's chromosphere line.
6240.86	*Fe*	7							Reversed? twice.
6243.06	*V*	10	3	6					
6243.32	*V*	11	3	7					
6244.03		5			3	−3			
6244.69		5			5	−3			Obliterated once.
6245.83		5			5	−4			Obliterated once.
6246.54	*Fe*	3	2	4					
6247.77	p*Fe*	6			6	−4			Young's chromosphere line. Enhanced iron.
6252.05	*V*	12	4	7					
6265.35	*Fe*	4	2	2					
6266.55	*V*	10	3	6					
6269.08	*V*	11	4	6					
6274.87	*V*	11	4	6					
6280.83	*Fe*	6	1	2					Generally hazy.
6285.38	*V*	11	3	5					

TABLE I—*Continued*

Wave-Length	Element	Spot Spectrum					Chromosphere		Remarks
		Total No. Obs.	Reversed		Weakened				
			No. Obs.	Inten.	No. Obs.	Inten.	No. Obs.	Inten.	
6291.18	*Fe*	1	1	2					
6296.58	*V*	11	6	8					
6301.72	*Fe*	6	1	1					Young's chromosphere line.
6302.71	*Fe*	10	7	10					Young's chromosphere line.
6318.24	*Fe*	1			1	−2			Young's chromosphere line.
6319.46		2			2	−3			
6322.91	*Fe*	2	1	4					
6327.82	*Ni*	4	1	5					
6330.32	*Cr*	11	8	9					
6331.06	*Fe*	8	2	4	1	−2			
6337.05	*Fe*	10	7	5					Young's chromosphere line.
6347.31		5			5	−4			Obliterated once. Young's chromosphere line.
6358.90	*Fe*	7	4	4					
6363.09	*Cr–Fe*	11	5	9					
6369.68	*Fe*	1			1	−4			Young's chromosphere line.
6371.57	*Fe*	2			1	−4			Young's chromosphere line.
6400.54	*Fe*	8	4	6					
6415.20		3			3	−4			
6417.13	*Fe?*	1			1	−4			Young's chromosphere line.
6420.17	*Fe*	3	1	5	2	−2			
6432.89	*Fe*	7			7	−4	1	5	Generally obliterated in spot.
6450.03	*Ca*	2	1	5					
6455.82	*Ca*	9	1	7					
6456.60	p*Fe*	7			7	−4	1	5	
6475.85		5	1	?	1	−5			
6482.10		5	2	4					
6496.69	*Fe*	6			2	−3			
6499.17	*Fe*	10	5	7					
6516.31		1			1	−1	1	8	
6532.0	*V?*	11	1	5					
6546.48	*Ti–Fe*	1			1	−3			
6563.05	*H*						...	100	
6574.47		12	3	5					
6581.45		6	1	4					
6633.99	*Fe*	3	1	6					
6678.37	*He*						2	10	
6705.35		6	1	4					
6752.97	*Fe*	4	1	?	1	−2			
6842.29		1	1	4					
6842.95		3	3	6					
6881.98	*Cr*	5	1	5					
6882.78	*Cr*	5	1	5					
6883.33	*Cr*	5	1	4					

The table, as already stated, contains the results of both sunspot and chromospheric observations.

Columns 1 and 2 give the wave-lengths and probable origin of the various lines. Enhanced lines are indicated by "p," in accordance with Lockyer's and Fowler's notation.

Column 3 gives the total number of observations of the line in the sun-spot spectrum.

Column 4 gives the number of times that the line was seen reversed; while column 5 indicates the mean intensity or degree of the reversal, 10 being the maximum.

Column 6 gives the number of times that the line was recorded weakened or diminished in intensity. Column 7 gives the amount of this diminution, −5 indicating that the line is obliterated.

Columns 8 and 9 give the number of chromospheric observations of the line, and the mean intensity; the latter being based on Professor Young's scale as nearly as possible.

Column 10 is devoted to general remarks.

For convenience this table can be summarized as follows:

TABLE II

Element	Reversed	Weakened	Chromosphere*	Reversed and Chromosphere	Reversed and Weakened	Weakened and Chromosphere	Reversed, Weakened and Chromosphere	Totals
Iron	51	25	34	..	11	8	1	130
p Iron	..	..	5	..	..	4	..	9
Chromium	20	4	4	1	1	3	1	34
Titanium	10	2	3	..	1	3	..	19
p Titanium	..	1	2	..	..	1	..	4
Vanadium	21	..	1	1	..	..	..	23
Manganese	10	1	1	..	..	..	..	12
Nickel	8	10	1	..	2	..	..	21
Silicon	..	5	1	..	..	..	..	6
Calcium	3	..	4	..	..	..	..	7
Magnesium	..	..	4	..	..	..	..	4
Cobalt	..	..	2	..	..	..	..	2
Lanthanum	..	1	1	..	..	..	..	2
Yttrium	1	..	3	..	..	1	..	5
Helium	..	..	3	..	..	..	..	3
Barium	..	..	3	..	..	..	..	3
Sodium	1	..	..	..	..	2	..	3
Hydrogen	..	..	1	..	..	..	..	1
Unknown	21	18	18	..	3	4	..	64
Totals	146	67	91	2	18	26	2	

* Young's chromospheric lines are not included in this table.

The columns in this table are mutually exclusive, hence, for example, to find the total number of chromospheric lines due to any element, it is necessary to add the figures standing opposite to that element in columns 4, 5, 7, and 8.

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THE CHEMICAL REACTIVITY OF THE CARBONYL GROUP AS MEASURED BY ITS ABSORPTION SPECTRUM

By A. W. STEWART[1] and E. C. C. BALY

The question as to how far the space relations of atoms within a molecule could affect the properties and reactions of certain compounds was first raised twenty years ago by Wislicenus, and since that time the problem has attracted the attention of many chemists and physicists. Yet, in spite of the great interest which it has aroused, it cannot be said that very great progress has been made in some branches of the subject. An example may be chosen from the work of Menschutkin upon the esterification of aliphatic acids.

By a series of measurements he was able to show that, while a simple acid esterified with ease, the derivatives of the same acid, which were formed by the substitution of methyl groups for hydrogen atoms in the original compound, were much more difficult to esterify. The velocity of esterification was proved to be quite independent of the affinity constant of the acid used, as the following table shows:

Name of Acid	Formula	Velocity of Esterification	Affinity Constant
Acetic	$CH_3.COOH$	3.661	0.00180
Propionic	$CH_3.CH_2.COOH$	3.044	0.00134
Isobutyric	$(CH_3)_2CH.COOH$	1.0196	0.00144
Trimethyl-acetic	$(CH_3)_3C.COOH$	0.0909	0.00098

The most obvious explanation for this phenomenon appeared to necessitate the assumption that the volumes of atoms were not negligibly small when compared with their intramolecular paths of vibration. If this assumption be made, the phenomenon of hindrance can be understood and the cause explained in the following manner. The esterification process requires that the alcohol molecule involved in the reaction should approach very closely to the carboxyl radicle of the acid used. Such an approach will be

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easy, so long as the groups attached to the carboxyl radicle are not bulky. This is the case in acetic acid. But if for the hydrogen atoms in the acid nucleus we substitute methyl radicles, which are much greater in volume, the alcohol molecule will find much greater difficulty in forcing its way into the neighborhood of the carboxyl group, just as a person would find greater difficulty in walking into a crowded room than into a sparsely filled one.

There can be no doubt that, if atoms have any size at all, this theory of "steric hindrance," as it is called, will hold good; but it cannot be proved that the effects attributed to this cause play any very considerable part in the reactions in question. It seems more probable that the free paths of the atoms in their intra-molecular vibrations are so large in comparison to the size of the atoms themselves that this heaping up of substituents in the neighborhood of the reactive group would have no very marked effect.

Stewart[1] has shown that, when a hydrogen atom near the carbonyl group of a ketone is replaced by a methyl radicle, the result is a decrease in the additive capacity of the carbonyl group. This might have been anticipated from the hypothesis of steric hindrance, since the volume of the methyl radicle must be greater than that of a hydrogen atom. A contradiction between theory and experiment is found in the case where, instead of a methyl radicle, a $-COOEt$ group is introduced into the molecule. In the case of the latter group it is found that, instead of decreasing the velocity of addition of sodium hydrogen sulphite, as its bulk might lead us to predict, it has the contrary effect; for some of these ketones which contain a carboxyl group are much more reactive than the corresponding simple ketone, and, *a fortiori*, than the methyl substituted ketone. The figures found for acetoacetic ester, acetone, and methyl ethyl ketone show this clearly:

		10	20	30	40 Min.
Acetoacetic ester.....	CH_3COCH_2COOEt	37.4	47.0	56.0	60.0
Acetone.....	CH_3COCH_3	28.5	39.7	47.0	53.6
Methyl-ethyl ketone	$CH_3COCH_2CH_3$	14.5	22.5	25.1	29.1

The figures give the percentage of bisulphite compound formed

[1] *Chem. Soc. Trans.*, **87**, 185, 1905; *Proc.*, **21**, 78.

by each ketone during the time indicated. It is thus made evident that some new influence has come into play, which tends to mask or modify the steric hindrance due to the more voluminous group.

The carboxyl group in itself, however, is not sufficient to produce this increased reactivity of the carbonyl radicle, as the rate of addition of sodium hydrogen sulphite to ethyl laevulate $CH_3.CO.CH_2CH_2.COOEt$ was found to be slightly lower than that found in the case of methyl propyl ketone $CH_3.CO.CH_2CH_2.CH_3$, which contains a carbon chain of the same length; and a like result was observed in the case of the diketone acetonyl acetone $CH_3.CO.CH_2.CH_2.CO.CH_3$. On the other hand, acetone dicarboxylic ester $COOEt.CH_2.CO.CH_2.COOEt$ has an additive capacity even greater than that of ethyl aceto-acetate. Acetone shows very little sign of tautomeric change; while, on the contrary, acetoacetic ester and acetone dicarboxylic ester are tautomeric compounds. Thus here again theory and experiment appear to be opposed to one another, the true carbonyl compound having much less reactive power than the semi-enolised body. It occurred to us that in this fact was to be found the key of the problem, and that the exceptionally great reactivity of the carbonyl group in tautomeric compounds was due to the actual process of tautomeric change. Acetoacetic ester, under conditions, exists as an equilibrium mixture of the two bodies (I) and (II); and the conversion of the first into the second, and vice versa, is going on continuously.

(I) $CH_3-\underset{\underset{OH}{|}}{C}=CH-COOEt$ (II) $CH_3-\underset{\underset{O}{\|}}{C}-CH-COOEt$.

Now, when a molecule of (I) is converted into a molecule of (II), the result is the formation of a carbonyl group from a hydroxyl group. From analogy with the behavior of atoms in the nascent condition, we must suppose that this "nascent carbonyl group" is endowed with a much greater reactivity than that possessed by the ordinary non-nascent carbonyl radicle. This activity need not, however, be occasioned purely by the actual wandering of the hydrogen atom from the oxygen to the carbon; it may be due to some finer play of forces within the molecule which manifests itself in the production of the characteristic absorption of the acet-

oacetic ester spectrum. The condition into which the hydrogen atom is thrown as a result of this play of forces may be termed a condition of "potential tautomerism," and in it the hydrogen atom will possess a reactive power more or less analogous to that required by an atom as a consequence of the ionisation process.[1]

If we now apply this idea to several cases which have hitherto been classed under the head of steric hindrance, it will be found that they can be satisfactorily explained. Taking the case of the ketones which have already been dealt with by one of us,[2] a marked decrease in the reactivity of the carbonyl group is shown when the hydrogen atoms of acetone are successively replaced by methyl radicles.

In the course of their investigations of the spectra of derivatives of acetoacetic ester, Baly and Desch[3] proved that the equilibrium between the enolic and the ketonic forms produces an absorption band in the ultra-violet region of the spectrum; and they also showed that this band is not due to the shifting of a hydrogen or metallic atom, but is rather to be considered as the result of some intra-atomic change. In the hope of finding some analogous process in the simple ketones, we examined the absorption spectra of several; and we found that a similar absorption band exists there as well. We further noticed that *the persistence of this band decreases proportionately to the diminution in the reactivity of the ketone's carbonyl group.*[4]

For instance, the following figures show the percentages of oxime formed by various ketones in twenty minutes;[5] and on comparing these amounts with the curves of the absorption spectra shown in Fig. 1, the relation between the two will be evident.

	% Oxime Formed
Acetone, CH_3COCH_3	49·7
Methyl ethyl ketone, $CH_3COCH_2CH_3$	39·2
Methyl propyl ketone, $CH_3COCH_2CH_2CH_3$	37·3
Methyl iso-propyl ketone, $CH_3COCH(CH_3)_2$	31·5
Pinacoline, $CH_3.CO.C:(CH_3)_3$	17·0

[1] Baly and Desch, *Astrophysical Journal*, **23**, 110, 1906.

[2] Stewart, *loc. cit.*

[3] *Loc. cit.*

[4] The method of observing and plotting the curves of absorption spectra was described in the previous paper (*Astrophysical Journal*, **23**, 110, 1906).

[5] Stewart, *Chem. Soc. Trans.*, **87**, 410, 1905.

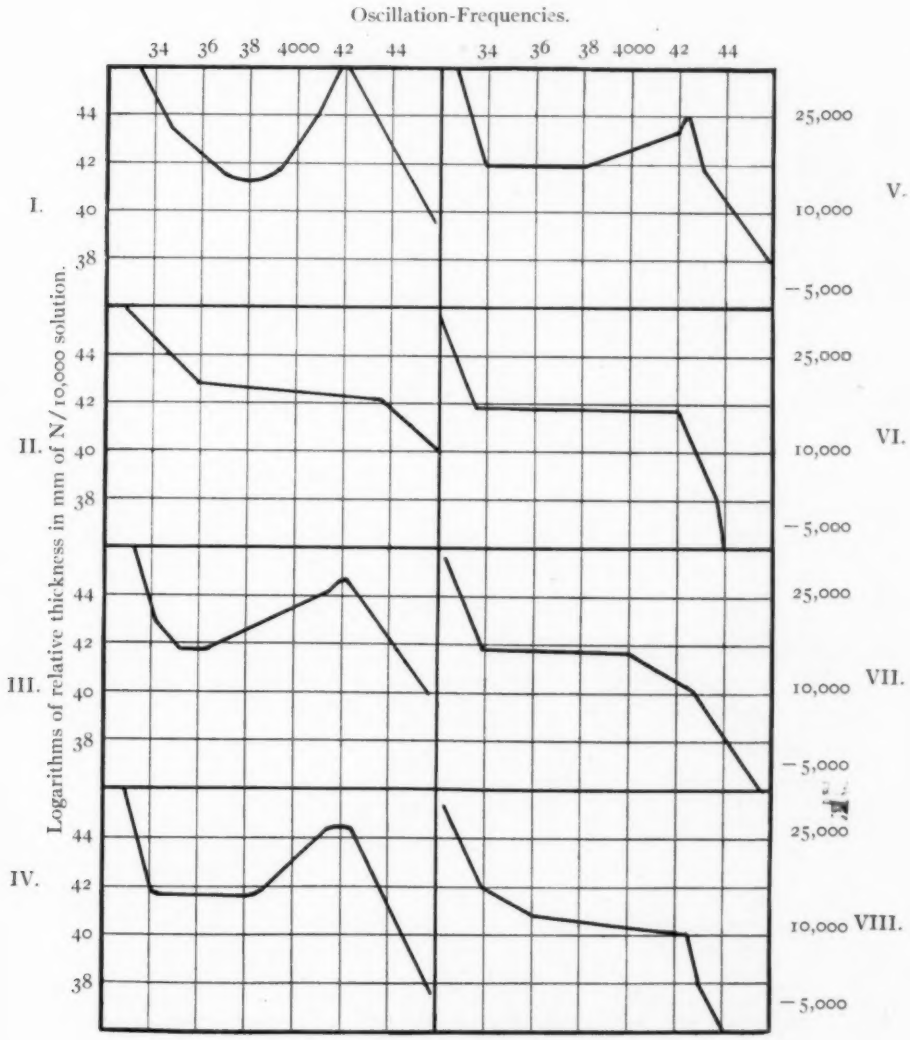


FIG. 1

I. Acetone.
II. Acetone (in water).
III. Methylethyl Ketone.
IV. Methyl propyl Ketone
V. Methyl iso propyl Ketone.
VI. Pinacoline.
VII. Methyl hexyl Ketone.
VIII. Methyl nonyl Ketone.

Lapworth[1] showed that the action of halogens upon acetone was preceded by the production of the enolic form of the ketone; and he found, further, that the presence of acids hastened the reaction. Now, he had already shown[2] that the presence of acids brings about a rapid attainment of equilibrium between the tautomeric forms of carbonyl compounds; or, in other words, the addition of acid has a tendency to produce a "nascent carbonyl group." Hence, in the case of acetone itself, not only is there direct spectroscopic evidence in favor of tautomeric change, but the chemical evidence at our disposal is also favorable. Instead of attributing Lapworth's results to the actual formation of the enolic form and an immediate addition of halogen, we prefer to look at them from another point of view. It is obvious, if we consider the change of the group $-CH=CH(O\overset{*}{H})-$ into $-CH\overset{*}{H}-CO-$, that the hydrogen atom marked with an asterisk must become "pseudo-nascent" in the process of change. It would therefore be peculiarly liable to chemical action, and would easily be replaced by halogens. The very great ease with which the methylene hydrogen atoms in acetylacetone are replaceable by halogens lends further support to our hypothesis.

In their paper Baly and Desch (*loc. cit.*) stated that acetonylacetone and ethyl laevulate were pure ketonic substances; but on examining the spectra of these substances at greater concentrations than were previously employed, we have been able to detect at one point a rapid extension of the spectrum which corresponds to a very shallow absorption band (Fig. 2). The shallowness of the band indicates that the tautomerism in these two compounds is very weak, which agrees with what has been found with regard to the reactivities of their carbonyl groups. The close agreement between theory and experiment in these cases is very noteworthy.

Now Petrenko-Kritschenko has shown[3] that the speed of phenylhydrazone formation is greatly influenced by the nature of the solvent in which the reaction is carried out. It appeared probable to us that this might be due to the influence of the solvent upon the

[1] *Chem. Soc. Trans.*, **85**, 32, 1904.

[2] *Ibid.*, **81**, 1503, 1902 and **83**, 1121, 1903.

[3] *Journ. Russ. phys.-chem. Soc.*, **35**, 404, 1903.

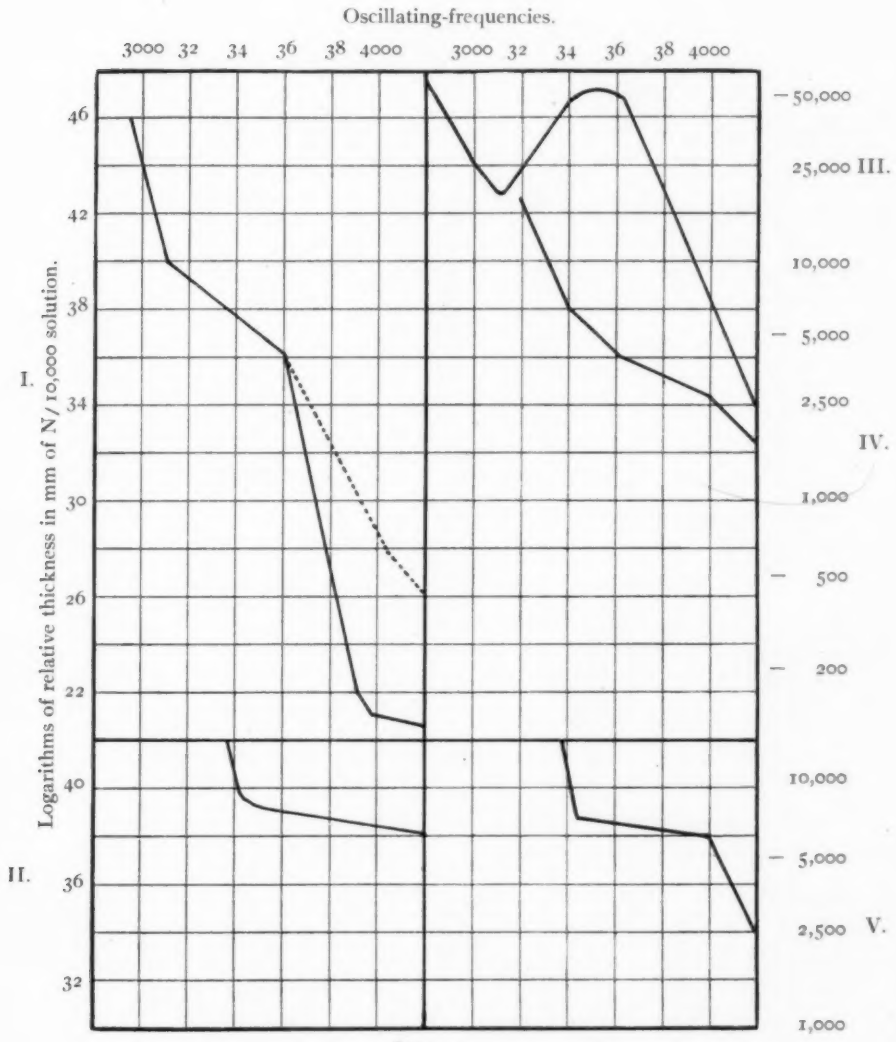


FIG. 2

I. Acetoacetic ester in alcohol (full curve).
The same in water (dotted curve).
II. Ethyl laevulate.
III. Ethyl pyruvate.
IV. Ethyl diethyl aceto acetate.
V. Acetonyl acetone.

tautomerism process; and to test the matter we examined the spectra of acetone and acetoacetic ester in aqueous solution, using as a control in the latter case the spectrum of diethylacetoacetic ester, which is much less tautomeric than the parent substance. From the curves for acetone in alcoholic and aqueous solution it will be seen that the influence of water is very marked, the band in the latter case being much shallower than in the former. The three curves shown in Fig. 2 give the absorption spectra of the acetoacetic ester series; and it is obvious from them that the water has reduced the tautomerism very considerably. It is probable that the greater the unsaturation of the solvent, the less reactivity will be shown by the carbonyl group of the dissolved ketone.

The evidence from simple ketones being so far favorable, we must now examine the case of ketones containing an ethyl carboxylate group. If tautomeric change alone were the cause of the reactivity of the carbonyl radicle, compounds containing the group $-CO-CH_2-CO-$ should be more reactive than those which do not contain it, and the reactivity of the carbonyl group in pyruvic ester ($CH_3COCOOEt$) should not be at all abnormal, since the group in question does not occur in it; if, however, the reactivity were found to be great in this case, we hoped that some light might be thrown upon the problem by the study of the compound's spectrum.

We therefore decided to compare the rates of addition of potassium hydrogen sulphite to acetone, acetoacetic ester, acetonedicarboxylic ester, and pyruvic ester. The results obtained by the method employed are given in the table below:

		5	10	15 Min.
Acetone	CH_3COCH_3	5	7	9%
Acetoacetic ester	CH_3COCH_2COOEt	12	18	24
Acetonedicarboxylic ester	$CO:(CH_2COOEt)_2$	30	36	42
Pyruvic ester	$CH_3COCOOEt$	52	64	76

In spite of the precautions taken, these numbers are probably not quite accurate, owing to various causes which cannot be controlled; but the differences between the numbers themselves are very much larger than any possible experimental error under the conditions employed.

An examination of the figures shows that the introduction of a

$-COOEt$ group into acetone increases the additive capacity of the carbonyl group; the introduction of two $-COOEt$ groups still further enhances the reactivity of the carbonyl group; but the most striking effect is produced when, as in the case of pyruvic ester, the carbonyl and carboxyl groups are brought into juxtaposition in the chain. Now, in the case of pyruvic ester, though the compound does sometimes react in the enolic form, it is most improbable that the change of the enolic into the ketonic form is going on at a rate at all comparable to that in which it is occurring in acetoacetic ester or acetonedicarboxylic ester, so that it is not likely that the exceptional reactivity of the carbonyl group in pyruvic ester is due to this kind of tautomerism.

We thought it advisable to examine the spectrum of pyruvic ester, in the hope that some light might thus be thrown on the problem of the activity of the carbonyl group. We found that pyruvic ester gives an absorption band which lies much nearer to the red end of the spectrum than the band given by acetoacetic ester. The origin of the band in the pyruvic ester spectrum might be looked for in two phenomena; either in the enol-keto change of the group CH_3-CO-, or in the interaction of the carbonyl and carboxyl groups of the radicle $-CO-COOEt$. The first explanation is impossible, since, if the band were produced by a similar state of intra-atomic vibration in both instances, it would occur in nearly the same place in the spectrum, while actually the new band has its head with a frequency of 3100, while that of the acetoacetic ester band lies at 3700. Further, since the molecule of pyruvic ester is lighter than that of acetoacetic ester, we should expect to find the band in the latter case nearer to the red end of the spectrum than in the former; while actually the reverse of this is observed.

In order to make certain that the band in question was actually produced by the proximity of two true carbonyl groups in the chain—i. e., that it was not due to the $-COOEt$ group of the carboxylate radicle—we examined the spectra of several α-diketones and found a similar band in all of them, though in them it was situated nearer the red end of the spectrum. For example, in the case of camphorquinone $C_8H_{14}\begin{cases} C=O \\ | \\ C=O \end{cases}$ (Fig. 3) it will be seen that an absorption

band is shown which has a very long persistence. Its head lies at a frequency of 2070.

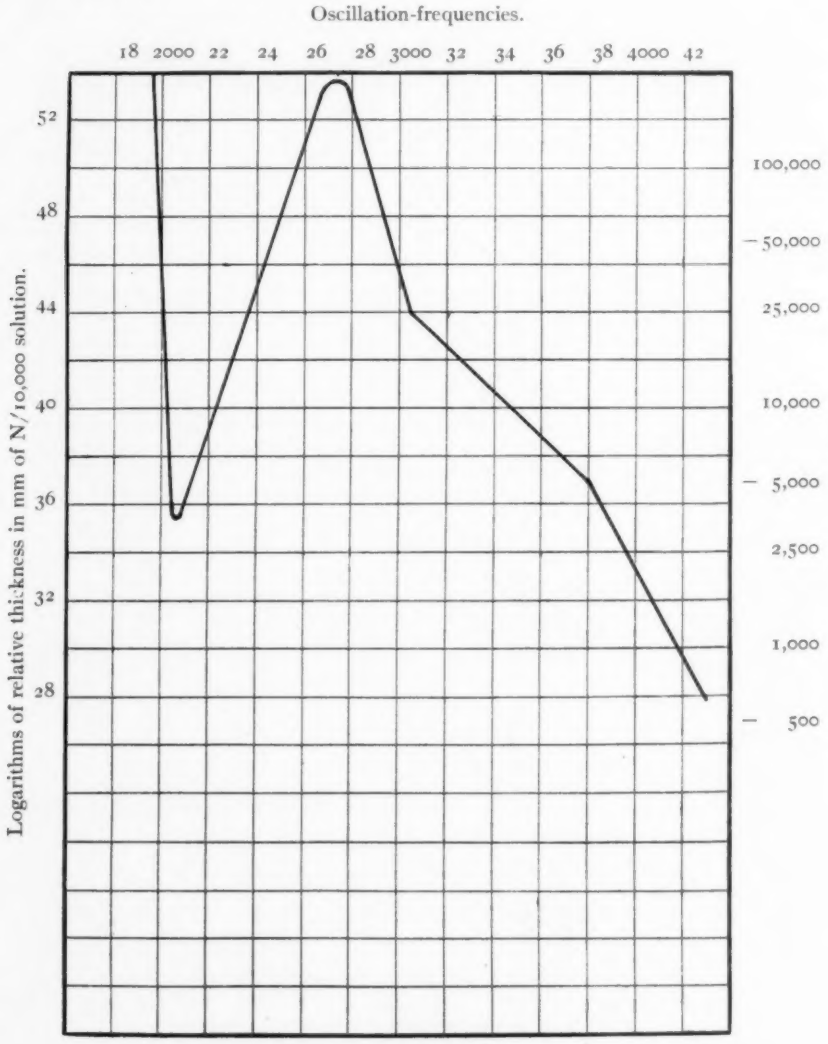


FIG. 3.—Camphor quinone.

It was thus proved that the type of band in question was due to the two carbonyl groups in the *α*-position to one another. It has already been pointed out that Baly and Desch concluded that,

though the keto-enol absorption band was produced by intra-atomic vibration, it was caused by the change of linkage brought about by the oscillation of the hydrogen atom during the change from the ketonic to the enolic form. From analogy we should expect to find a somewhat similar state of things in the present case. Now, the only possible way in which such a change of linkage can be supposed to occur in pyruvic ester is by imagining that, like acetoacetic ester, it occurs in two forms:

$$\text{(I)}\quad CH_3-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-OEt \qquad \text{(II)}\quad CH_3-\underset{\underset{O-O}{|\ \ |}}{C=C}-OEt$$

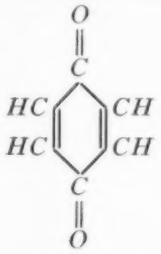
It is very hard to indicate exactly what is meant by the aid of the usual structural formulæ, as they only indicate a static condition of the molecule, while what we wish to suggest is essentially a dynamic state. We wish to make it perfectly clear that we do not suppose these two forms necessarily to exist statically; but, owing to the defect of ordinary structural formulæ, it is impossible to write them otherwise if the usual symbols be employed. Our conception can best be comprehended if it be clearly borne in mind that the two formulæ are not intended to represent actual compounds, but merely two phases of the same compound. If this conception of phases be understood, it will be apparent that the change of linkage is continually going on, and that this change will affect the intra-atomic relations of the molecule very much in the same way as they are affected by the phenomena of tautomerism.

At the same time, it should be noticed that the change of linkage from (II) to (I) would produce what we have already defined as a "nascent carbonyl group" which would have great reactivity. Thus we are led to conclude that substances which show these peculiar absorption bands will in general be more active chemically than other compounds which do not exhibit such selective absorption.

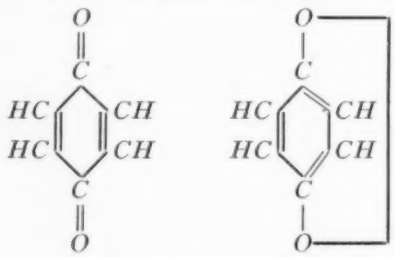
The idea which we have put forward cannot be considered as part of the theory of tautomerism, as, owing to its associations, the name "tautomerism" will always suggest the wandering of a hydrogen atom. It is unfortunate that the name "Desmotropism" has already been employed to denote tautomerism, as it seems well fitted to describe the phenomenon with which we have dealt. We

therefore wish to propose the word "Isorropesis" (*ἰσορροπεια*, "equipoise") to describe the process.

The arguments in favor of this theory appeared to us to warrant its application to other classes of compounds, and we proceeded to make a further series of investigations, some of which will be dealt with in a later paper. For the present, quinone



is the only compound which need be described. The known close relation to one another in which the two para-positions in benzene stand, seemed to lend probability to the idea that a band somewhat similar to those observed in compounds containing the group $-CO-$ $-CO-$ might be found in the spectra of the para-quinones. Our anticipations were again justified, as the quinone spectrum has a band almost identical with that of camphor quinone, its head lying at 2150 (see Fig. 4). Now, it is known that quinone can exist in two forms, for both of which chemical evidence has been adduced:



It appears not unwarrantable to assume that in this case also the absorption band is caused by the "make and break of contact" between the two oxygen atoms, as already suggested for pyruvic ester. Thus it may be concluded that the actual wandering of a hydrogen atom is not necessary for the production of these absorption bands. Again, since the result of this "make and break"

would be the production of two nascent carbonyl groups, an explanation is thus given of the great chemical activity of the carbonyl radicles in quinone.

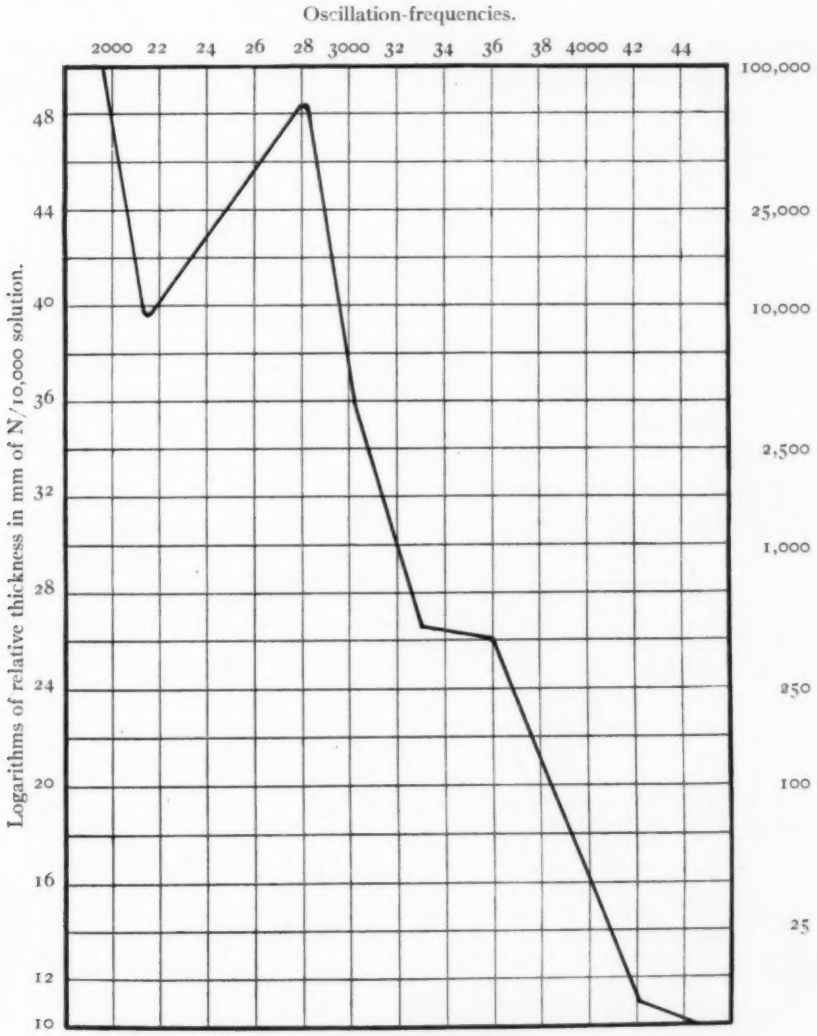


FIG. 4.— Quinone.

It is thus proved that the two carbonyl groups in the *a* position to one another give rise to a new type of absorption band. From

analogy with Baly and Desch's observations that the ultra-violet absorption bands are produced by the change of linkage brought about by the oscillation of the hydrogen atom in the process of enol-keto tautomerism, we should expect to find a somewhat similar change of linkage in the α-diketones. We propose to reserve a full discussion of this process to a further paper in connection with its relation to color, but it may be stated that we are undoubtedly concerned with the residual affinity upon the two oxygen atoms. The free period giving rise to the absorption band is due to a mutual disturbance or an oscillation between these residual affinities.

It would seem that the results described above are of considerable importance, for they show that the chemical reactivity of a ketonic compound can be measured directly by means of the spectroscope. We find that the persistence of the absorption bands given by these compounds is directly proportional to their chemical reactivity. It is a logical conclusion that the chemical reactivity of these compounds is due to a change of linkage within the carbonyl group of the ketone. This change of linkage may either be produced by a wandering hydrogen atom such as occurs in the reversible equilibrium

$$-CH_2-C- \qquad -CH=C-$$
$$\qquad\quad \| \qquad\qquad\quad |$$
$$\qquad\quad O \qquad\qquad\quad OH$$

which occurs or tends to occur in the monoketones and the β diketones containing the $-C-CH_2-C-$ group, or it may be produced

$$\qquad\quad \| \qquad\quad \|$$
$$\qquad\quad O \qquad\quad O$$

by isorropesis or the oscillation between the residual affinities of two carbonyl oxygen atoms in juxtaposition, thus

$$-C-C- \qquad -C=C-$$
$$\quad \| \ \| \qquad\quad | \ |$$
$$\quad O \ O \qquad\quad O-O$$

Furthermore, it is evident that all measurements of the chemical reactivity of a ketonic compound are simply measurements of the amount to which tautomerism is present in the compound. A very great deal of importance has been attached to these measurements in connection with the theory of steric hindrance, but our results, we are sure, will go far to discountenance this theory. There

is no doubt that the decrease in chemical reactivity caused by the substitution of hydrogen atoms by groups of atoms is caused, not by the bulk of these atoms, but simply by the fact that fewer hydrogen atoms are available for the tautomeric processes. It is unnecessary to cite in this place the many reactions of ketones which have been measured in support of the theory of steric hindrance, but there is no doubt that they can all be explained more easily and more rationally by the conception of the nascent carbonyl group set forth above.

The method employed for the photography of the absorption spectra of the substances, as mentioned above, has already been described;[1] the compounds were in each case prepared most carefully and satisfactorily answered every test of their purity. Except where especially mentioned to the contrary, the absorption spectra of the substances were observed in alcoholic solution.

CONCLUSIONS

1. The reactivity of any carbonyl group is not inherent in the group itself, but is produced by the action of neighboring atoms upon the carbonyl group rendering it "nascent."

2. Such action may take the form of tautomerism, or of a modification of tautomerism which does not require the actual transfer of a hydrogen atom from one atom to another, but merely some intra-atomic disturbance in the system $-CH_2-CO-$.

3. The action may also take the form of the process which we have termed "isorropesis," in which no actual wandering of the atoms occurs, but in which some oscillation between the residual affinities of the oxygen atoms of the two carbonyl groups is involved.

4. Many cases which at present are accounted for on the hypothesis of steric hindrance can be better accounted for either by tautomerism or isorropesis; and some cases which are in direct contradiction to the steric theory can also be explained. It is therefore claimed that the hypothesis of the "nascent carbonyl group" accounts more satisfactorily for the facts and is superior to explanations based upon the idea of steric hindrance.

5. When the possibility of the formation of a nascent carbonyl

[1] Baly and Desch, *loc. cit.*

group is excluded, neither the usual ketonic reactions nor an absorption band is observed. The carbonyl radicle may then be considered an "inactive" carbonyl group in contradistinction to a "nascent" one.

6. Inasmuch as both the processes of tautomerism and isorropesis result in the appearance of an absorption band whose persistence is a measure of the amount to which these processes are taking place, it is possible to determine the chemical reactivity of a ketonic compound by observing the persistence of the absorption band.

In conclusion we wish to express our thanks to the Chemical Society of London for a grant toward the expenses of this research; to Professor Collie and Dr. Smiles, for the great interest they have taken in the work; and to Mr. W. B. Tuck, B. Sc., for assistance during the course of the investigation.

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LINE STRUCTURE, III.

RELATION OF WIDTH TO INTENSITY OF NORMAL LINES

By P. G. NUTTING

That the spectral width of normal spectrum lines varies with the nature of the excited gas, the intensity of its excitation, and the pressure of the surrounding atmosphere is well known to spectroscopists. The class name "normal" lines is used to designate simple lines which merely broaden and reverse as their intensity is increased, as distinguished from "composite" lines consisting of several components when fully developed. A. A. Michelson[1] and F. L. O. Wadsworth[2] from the "visibility" of lines in the interferometer calculated their width and established relations between width and atomic weight and pressure. They appear to have taken no account of the effect of intensity on the width of lines and composite lines are treated as single lines.

The echelon grating, with its high resolving power and direct reading property, exhibits the individual character of fine lines as does no other instrument. Structure, shading off at the edges, and the like are shown by the largest Rowland grating down to a line-width of about 0.05 t.-m; lines narrower than this appear merely as narrow ribbons of light without character. The echelon is just at its best at this width, and gives the details of lines as narrow as 0.005 t.-m.[3]

Previous work[4] having indicated the existence of an intimate relation between the width and structure of arc lines and their intensity, a spectrophotometric study of line width was undertaken. The plan was to measure width and intensity simultaneously, the former with an echelon provided with a micrometer eyepiece, the latter with a special spectrophotometer.

[1] *Phil. Mag.*, (5) **34**, 280–299, 1892.

[2] *Astrophysical Journal*, **6**, 30, 1897.

[3] P. G. Nutting, "Line Structure, I," *Astrophysical Journal*, **23**, 64–78, January 1906; "Line Structure, II," *ibid.*, 220–232, April 1906.

[4] Most lines are so sharp and well defined when narrower than 0.1 t.-m. that width measurements to within the width of the finest cross-hairs are easily made.

The apparatus was used as shown in the figure. Light from the source passed by one path through a dispersing apparatus and echelon, and by another path through a spectrophotometer so placed that its ocular was very near the echelon ocular. A 1 mm horizontal slit placed near the arc served to screen off all light except that from the central portion of the luminous flame, and the same portion supplying the light entering the echelon. A Nernst lamp at normal voltage, checked at intervals with a normal Hefner, served as reference standard. The light from the Nernst lamp entered the 0.2 mm spectrophotometer slit between the two right-angled prisms through which the light from the arc entered. An ocular slit cut down the central continuous spectrum to the width of the spectrum lines seen above and below it. The echelon ocular micrometer was fitted with diagonal quartz-fiber cross-hairs.

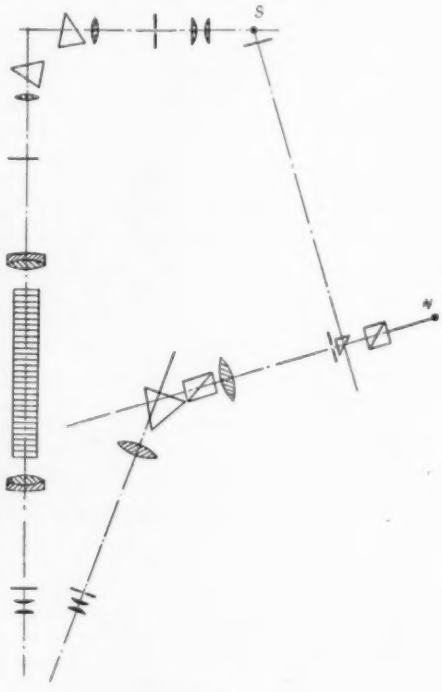


FIG. 1

The lines investigated were chiefly the brighter visible arc lines with a few Plücker tube lines. Of these attention was directed toward the normal lines—lines which show no permanent structure, but simply broaden and reverse with increase of intensity. Leaving out of account spectra filled with excessively numerous lines, fully one-third of the spectrum lines possess permanent structure, many are triple, some double, and some quadruple. Once composite, always composite, appears to be generally true; that is, a line showing structure under any conditions will appear composite under all conditions. A line which is (say) triple in a Plücker tube will be

found triple in the arc spectrum. Components differ in width and relative intensity under different conditions of production just as the lead spark spectrum varies with capacity and inductance used, but a composite line always retains its individuality as does the lead spectrum.

When a line is really composite, the fainter components disappear *in situ* as the intensity is decreased; if it is a normal single line reversed, the wings merge in a single line with decrease in intensity. The spectrum of manganese beautifully illustrates the distinctions involved. In the green, in the midst of a multitude of normal lines, are a dozen double and triple lines. These really composite lines remain as steady as though painted, while their neighbors broaden and reverse with every flash of the arc.

Copper λ 5782 and λ 5700, and calcium λ 5858, are the most striking examples of permanent double structure, while zinc, cadmium, and the alkali metals have many striking triple and multiple lines. Of the normal lines good examples may be seen in the spectra of barium, palladium, chromium and titanium.

A brief list of spectra is given below, with an indication of the character of the prominent lines:

Lithium: all five composite.
Sodium: D lines composite.
Potassium: all composite.
Rubidium: all (four red, seven green) composite?
Magnesium: all normal.
Calcium: half composite, half normal.
Strontium: all normal.
Barium: all normal.
Titanium, cerium, thorium, vanadium, chromium, molybdenum, tungsten and uranium: all normal.
Manganese: twelve green composite, all others normal.
Iron, cobalt, nickel, palladium, platinum, rhodium and osmium: all normal.
Copper: two yellow, two green composite, λ 5106 normal.
Silver: all composite.
Gold: all normal.
Iridium: blue normal.

Zinc, cadmium, mercury, thallium, tin, lead and bismuth: all the lines observed are composite, namely: zinc λλ 6263, 4810, 4722, 4680; cadmium, λλ 6438, 5086, 4800, 4676; mercury, λλ 5790, 5769, 5461, 4358, 4748, 4078, 4047; thallium, λ 5350; tin, λλ 5631, 4525; lead, λλ 6002, 4058; bismuth, λ 4722.

Roughly speaking, then, excepting calcium and manganese, the lines of all the spectra in which lines are excessively numerous are normal, while the lines of the simple spectra—except gold, indium, and magnesium—are composite. This paper is a discussion of the behavior of the normal lines. The composite lines are to be treated in a later paper.

The width of a normal line appears to depend, aside from the pressure, upon the intensity alone. When, for example, copper is fed into an arc with carbon electrodes, the line λ 5106 is of the same width at a given intensity as when copper electrodes are used. It is the same whether metallic copper or a copper salt is fed into a carbon arc. If, as a salt burns away, the current is increased to bring the intensity of a line up to its original value, its width also is restored. Nor is this ratio of width to intensity appreciably affected by the addition of an alien salt or metal to an arc. A line has less diffuse wings when produced in an oxyhydrogen flame than when produced in an arc, but it appears to possess the same mean width at a given intensity in the two cases.

The green mercury line has three satellites on the side of the primary toward the red. These three lines are the narrowest bright lines known to the writer, and the middle one of these was for this reason chosen to verify the correction for slit-width to be applied to the measured width of a line. The figures quoted below and the points on the accompanying graph are from the first set of readings taken:

Slit-Width	Width of Line	Width of Slit	Slit-Width	Width of Line	Width of Slit
5.4	121 μ	114 μ	4.8	53	44
5.3	110	94	4.7	39	34
5.2	98	84	4.6	26	24
5.1	91	74	4.5	15	14
5.0	79	64			
			4.4	faint	4
4.9	67	54	4.36	closed	0

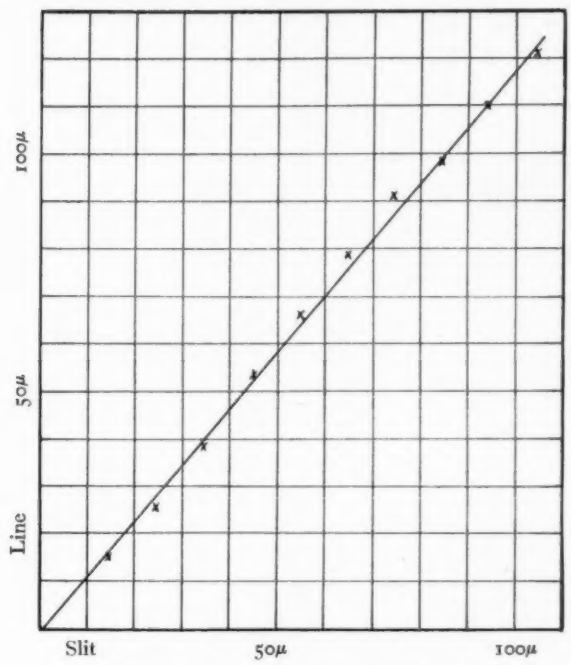


FIG. 2.— Width of Line: Width of Slit

Line-width and slit-width are seen to be proportional to each other far within the possible errors of measurement. The resolving power of the echelon is seen to be considerably (at least five times) greater than the calculated value of 0.01 tenth-meter. The actual width of the line itself is from the plot certainly not greater than 1 micron, or almost 0.001 t.-m. in terms of wave-length. In other words, the light of this satellite of the green mercury line is homogeneous to within 1 part in at least 5,000,000. The main primary of this line is fully twenty times as broad as this satellite, while the whole line, measured from extreme satellites, is three hundred times as broad, or about 0.3 t.-m.

The results of some observations on the relation of width to intensity of the yellow helium line λ 5876 are given below. They are the first and last of a series of observations. The helium was contained in short, stout Plücker tubes excited by means of a 5000-volt transformer. The intensity was varied by varying the current

in the primary. The two sets of observations quoted were made more than a week apart on two different Plücker tubes. The echelon slit was open 14 microns in one case and 24 microns in the other, the widths of the line being corrected by means of the plot reproduced in Fig. 2 above.

Tube 1			Tube 2		
Intensity	Slit-Width 24 μ		Intensity	Slit-Width 14 μ	
	Linear	Wave-Length		Linear	Wave-Length
1.0	42 μ	0.046 t.-m.	0.85	40 μ	0.044 t.-m.
1.9	47	0.052	1.44	46	0.050
3.2	57	0.062	2.6	56	0.062
4.7	66	0.072	3.9	64	0.071
6.7	76	0.084	5.0	69	0.076
9.5	93	0.102	6.0	72	0.079
12.9	109	0.120	7.1	75	0.083
19.0	115	0.126	9.0	77	0.085
			12.2	90	0.099
			20.2	115	0.126

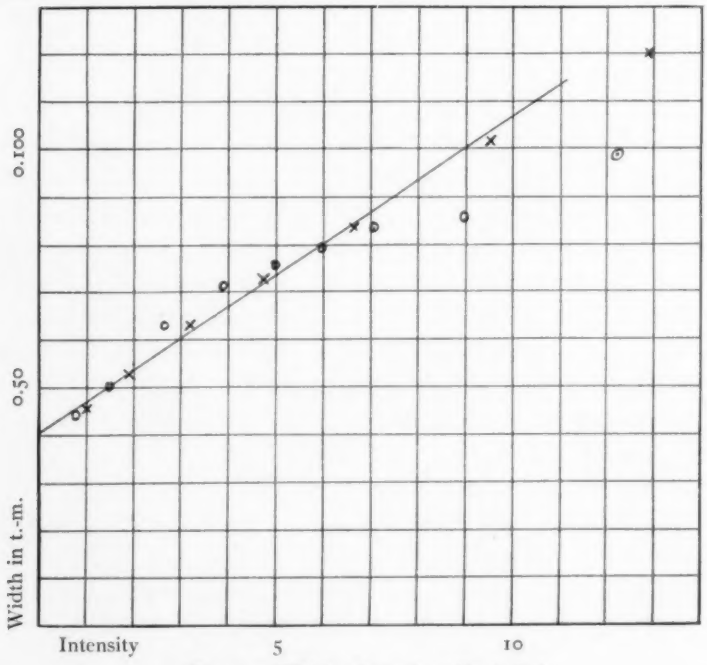


Fig. 3.—Width: Intensity, *He*, λ5876.

The width of the line is seen to vary considerably with its intensity, more than doubling within the range available. The relation between width and intensity is approximately linear for low and moderate intensities. At great intensities the width is, if anything, less than this proportionality would indicate. At the intensity called 10, the capillary of the tube was just commencing to burn and show sodium lines, and possibly this might account for the falling-off from the linear relation at high intensities, but arc lines show a similar falling off. Plotting against a quadratic or logarithmic abscissa does not help matters.

Extrapolating back to zero of intensity, there is good evidence that the line then possesses a finite width of perhaps 0.040 t.-m. Visual observation tends to confirm this, for at intensities much lower than the lowest at which the width can be measured with any accuracy, the line still appears as a ribbon of light rather than as a fine line. The appearance of the line suggests that it is an unresolved composite. With exceptionally favorable conditions, I have seen a faint separation into two components. If the line had two components, each of zero width, this limiting width of 0.040 t.-m. would represent the distance between their centers.

A few normal arc lines are sufficiently isolated in their spectra and variable in intensity to permit fairly accurate observations of the width-intensity relation to be made. Arcs of from 2 to 8 amperes were used. As the arc fluctuated, the maxima and minima were found to be reasonably constant in intensity and to permit of measurement. The best of the results are given below in the form of linear equations between width W and intensity I. They are taken from the plotted curves, all of which were of the same general shape as that reproduced in Fig. 3. W is expressed in tenth-meters, and I in terms of an arbitrary unit such that the intensity of the bright green line *Fe* λ 5328 from an iron arc of 5 amperes in open air is about 0.5.

Ba	λ 6342	$W = 0.034 + 0.0030\, I$
Ni	λ 5477	$W = 0.032 + 0.0035\, I$
Fe	λ 5328	$W = 0.025 + 0.0045\, I$
Cu	λ 5106	$W = 0.033 + 0.0030\, I$
Pd	λ 5296	$W = 0.032 + 0.0040\, I$

For comparison may be added:

He λ 5876 . . . . . $W=0.040+0.007\,I$
Hg λ 5461 satellite . . . . $W=0.001$

The results for the arc lines show a striking uniformity, both in limiting width and in intensity coefficient. Other lines gave data so similar, and the accidental errors were so large, that it was found to be only duplicating work to take measurements on them, and only minimum width and intensity at reversal were recorded. With the arrangement used—echelon slit *perpendicular* to the spectrum lines formed by the preliminary dispersing apparatus—many lines were simultaneously in the field of view, so that, if any of the many hundred lines observed had possessed exceptional qualities, they would have been at once noticeable.

The minimum width of all normal arc lines produced at atmospheric pressure lies between 0.02 t.-m. and 0.05 t.-m. This width is of the same order as the width to be expected from the Doppler effect and the kinetic gas theory. For, if δ is the spectral width of a line produced by a source moving with a mean speed of u cm/sec., then if V is the velocity of light, $\delta/\lambda = 2u/V$. For air at room temperature and pressure u is usually taken as about 4.5×10^5 cm/sec., increasing with the square root of both temperature and pressure. Hence the width of a green line should be at least $\delta = 5000\times 2\times4.5\times10^4/3\times10^{10}=0.015$ t.-m. If the arc gases are at a temperature of 3000°, then this width should by the kinetic theory be multiplied by the factor $(3000/300)^{\frac{1}{2}}=3.16$, hence $\delta=0.015\times 3.16=0.047$ t.-m. Similarly for a red line at λ 7000, $\delta=0.034$ t.-m.

Reversing the argument, the widths observed indicated that only the thermal motions of the radiating particles are concerned in the broadening. The conduction of a current by the gas in the arc does not add greatly to the translatory motions which the particles of a gas would have in virtue of their high temperature alone. In other words, line-of-sight motions are unaffected by the current through an arc.

At low pressure an inclosed arc with electrodes of iron, copper, brass, and nickel were used. With nickel some observations were

obtained with a clear window without disturbing the photometric adjustments used in the previous work. For *Ni* λ 5477,

$$W = 0.006 + 0.007\, I\,,$$

with a large probable error on account of the great fluctuations and altered character of the arc flame. Other lines were observed to have roughly the same minimum width. From kinetic theory the width at 1 cm pressure should be $(1/76)^{\frac{1}{2}} = 0.11$ of the width of atmospheric pressure. The latter for λ 5477 at 3000° is 0.043 t.-m.; hence at 1 cm pressure should be 0.0047 t.-m., considerably less than the width observed.

INTENSITY AT REVERSAL

The intensity of the line when reversal just occurred was recorded in the case of about eighty normal lines in different spectral regions and belonging to a wide range of elements. The striking uniformity of these intensities led to their being plotted against wave-lengths as abscissæ. The plot (Fig. 4) showed a well-defined galaxy through which a median line could be drawn with some certainty. Owing to the enormous fluctuations in the arc at the reversing intensity, the

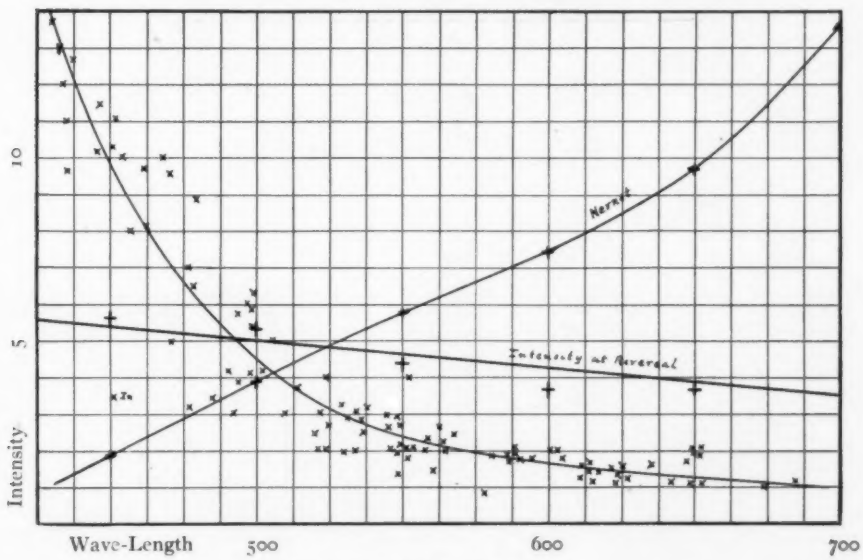


FIG. 4.— Intensity at Reversal

possible error in measurement is large, 20 to 60 per cent. But in view of the fact that the intensity of a line fluctuates by a factor of 10 to 100,000, measurements to within a factor of two are not unsatisfactory.

The points plotted in Fig. 4 relate to the Nernst lamp used as reference standard. Hence multiplication by the spectral energy of the Nernst lamp gives the relative energy of the various lines at reversal. The energy-curve for the Nernst lamp was obtained by inserting a Rubens thermopile before the ocular of the spectrophotometer.

Numerical data are given below. The thermopile was used with a Weston moving-coil galvanometer, and deflections are in millimeters. The 8-candle-power Nernst lamp, when operating at that luminosity, was found to have a drop of 106 volts across the filament, and was kept at this voltage to within 0.1 volt by hand regulation of the rheostat used as ballast for the lamp. At wavelength 650 the emission at 107 volts was 12 per cent. greater than at 106; at 105 volts, 15 per cent. less. The values of $dn/d\lambda$ used to reduce the prismatic to the normal energy-spectrum were specially determined for the prism used.

Wave-Length	400	450	500	550	600	650	700
Deflection of galvanometer	(3)	11	33	69	123	199	347
$dn/d\lambda$ (cm^{-1})	4000	2650	1780	1261	895	730	590
Normal Nernst spectrum	(120)	291	588	870	1101	1452	2048
Intensity of reversal (relative to Nernst)	(20.)	9.8	4.5	2.4	1.7	1.3	1.0
Intensity of reversal (corrected)	(240)	285	264	209	187	188	205

The actual energy intensity thus obtained is sensibly a constant, not only for all lines in the same spectral region, but for all lines in all regions. In other words, all normal lines reverse at the same intensity, provided of course that they are produced under similar conditions, say in an arc in open air. This constancy, if it be fully confirmed, will be of profound theoretical significance.

The constancy of this normal intensity is little, if any, affected by

1. The method of production within the arc, whether, e. g., salt or metal is introduced into a carbon arc, or electrodes of the pure or alloyed metal are used.

2. The element used. Iron, cobalt, and nickel points lie slightly below the median line, gold above, but these differences are well within the possible error in measurement.

3. Spectral series may affect the constancy, but only within the present experimental error. Most of the normal lines belong to non-series spectra. The five prominent gold lines, in particular, give a smooth curve.

Wave-Length	6278	5838	5230	5064	4793
Intensity Nernst	0.12	0.18	0.41	0.52	0.89
Actual intensity	103	124	197	214	267

4. Twinning[1] is not to be distinguished from reversal as regards the intensity at which it occurs. In so far as this fact is admissible evidence of the similarity of the two phenomena, it appears to indicate that all such reversal of arc lines is rather a real doubling in its early stages. At any rate, phenomena due to absorption and phenomena due to a doubling of the period of the radiator both occur, and probably together.

5. At low pressure, lines double or reverse at a considerably lower intensity. The components of the doublet being each much narrower than that at atmospheric pressure, they appear to separate when their centers are a smaller distance apart.

6. The components of composite lines appear to be capable of doubling, reversal, or multiplying like single lines, although this point will require considerable further study. There is so much overlapping that effects are difficult to observe except when components are well separated. Possible exceptions are the extremely narrow satellites like those of the green mercury line. These satellites broaden perceptibly when very intense, but show no trace of doubling or reversal.

The development of a typical normal line is then somewhat as depicted in Fig. 5, where frequency (or wave-length) is plotted against intensity. At high pressures (or temperatures), say in an open-air arc, the development of the line is shown by the full lines, at low pressures by the dotted lines. The intercept *ab* on the fre-

[1] See "Line Structure, II," *l. c.*

quency axis represents the minimum width or impurity of the spectrum line at a very low intensity. With increase of intensity, the line broadens and finally separates into two as the intensity corresponding to the point *c* is reached. With further increase in intensity the two components continually broaden and separate. At low pressure the minimum width is less and the line twins at a lower intensity.

There occur to me three possible explanations of this behavior of normal lines:

1. It may be an extreme type of reversal by absorption.

2. It may be an effect of the gas motion of the radiator on its elasticity, and hence on its frequency as discussed in "Line Structure, II."

3. A selective Doppler effect might give a doubling at certain intensities. Stark[1] finds that the canal rays give *displaced* rather than *broadened* spectrum lines, and hence concludes that only the swiftest particles emit light. Applied to arc spectra, this deduction would lead one to expect doubling.

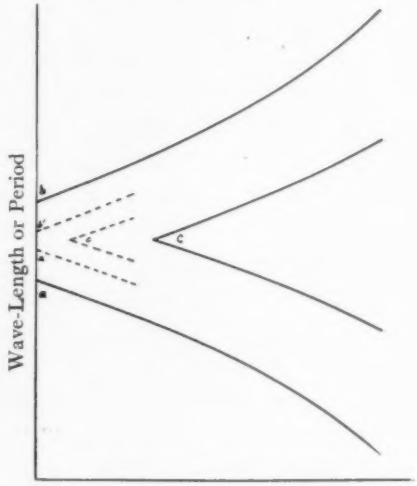


FIG. 5.—Wave-Length-Intensity.

There appears to be no conclusive evidence as yet for or against any of these three theories. It seems improbable that the doubling is an early stage of reversal proper on account of the extreme sharpness and brightness of its components. Dr. Humphreys unhesitatingly pronounced against reversal on viewing some of the twin iron lines through the echelon.

Assuming the Doppler effect, variability of speed and orientation are the two causes that would determine the character and behavior of single lines. Assuming the Maxwell-Boltzmann distribution for these and radiation independent of translatory motions of the radi

[1] *Physikalische Zeitschrift*, **7**, 251–256, April 15, 1906.

ators, a spectrum line would have as definite an energy-spectrum as a black body; observation, however, shows that lines possess an individuality indicating two or more parameters in the energy-period function.

If the character of the radiation is modified by the effect of rotation on the elasticity of the radiator, speed and orientation would be operative in broadening components as well as the original single line; components of a double line would be as broad or broader than the minimum width at small intensity (cf. Fig. 5). Distance between centers of components would be proportional to the speed of rotation, which is assumed proportional to the speed of translation. Orientation of translation would be without effect on the doubling of lines. These effects are in accord with observation.

Stark's theory that radiation occurs at the higher speeds of the radiator applied to the arc would eliminate part of the effect of speed of translation, leaving orientation fully operative—in direct contrast to the preceding. Minimum width would be zero. At all pressures width would be much more than proportional to intensity; doubling would occur only if axial radiation were relatively small, and even then would be diffuse. Still, this theory is attractive on account of its simplicity.

SUMMARY

1. Spectrum lines fall into two quite distinct classes, "normal" and "composite," only the latter showing permanent structure.

2. The spectral width of normal lines is approximately a linear function of their intensity.

3. The minimum width of normal lines at atmospheric pressure is approximately 0.04 t.-m., and is the same or nearly the same for all lines.

4. At low pressures the minimum width of normal arc lines was found to be about 0.005 t.-m. in the case of a few lines measured, with indications that all other normal lines were of the same minimum width at that pressure.

5. All normal arc lines double or reverse at the same (energy) intensity within a factor of two at most.

6. When doubling or reversal occurs, each component has approxi-

mately a width equal to the minimum width of the original line. In other words, normal lines twin when their width is increased to double their miminum width. After doubling, each component broadens very rapidly with increase in intensity, chiefly on its outer side.

7. Some, at least, of the components of the triple and other composite lines broaden and double with increase of intensity, like normal lines.

8. Three of the satellites of the green mercury line are mono-chromatic to within 1 part in at least 5,000,000 when produced at moderate intensity in an ordinary mercury lamp. That these satellites appear not to be subject to the Doppler effect is very remarkable.

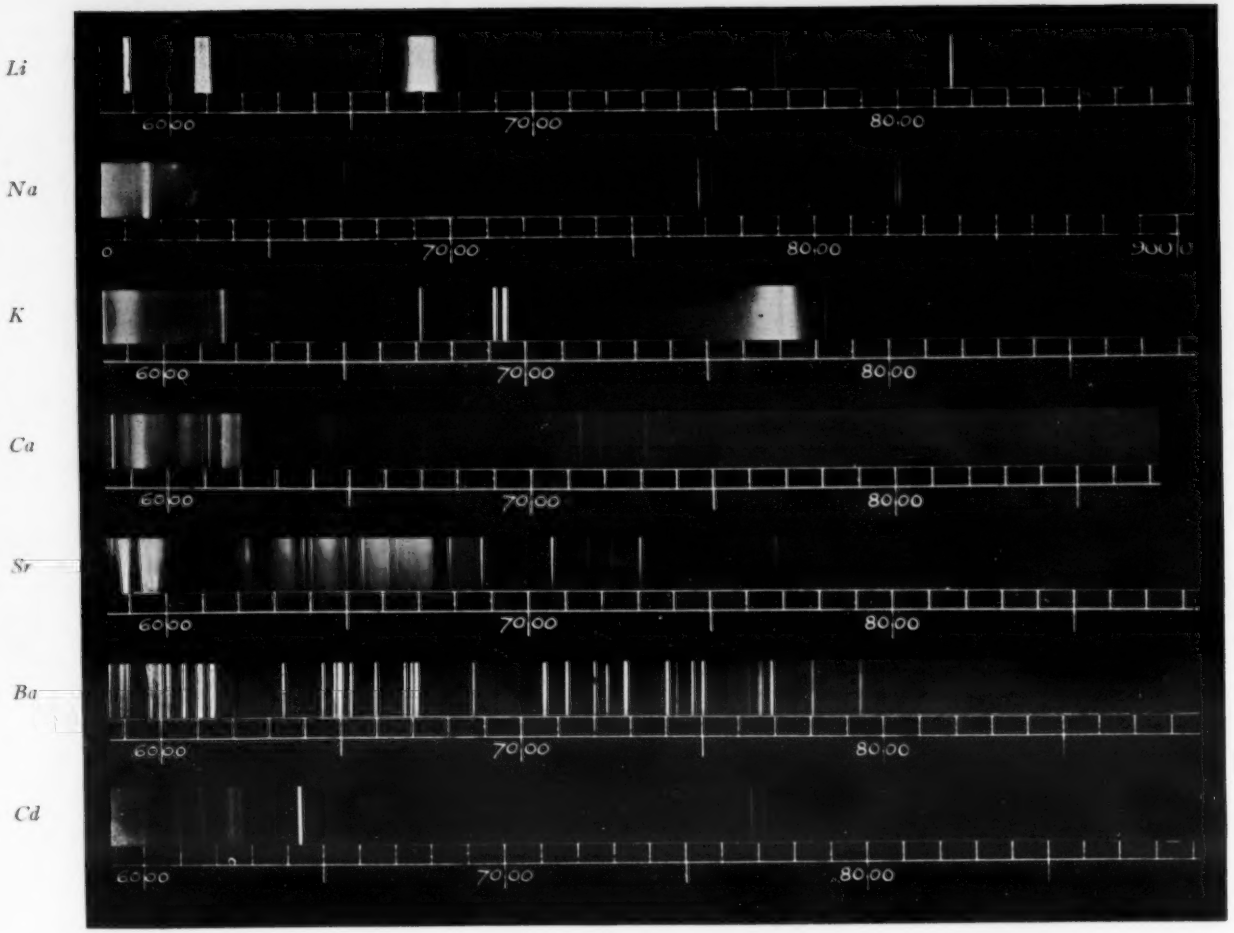
For absolute length standards, wave-length standards and interferometry as well, the narrowest possible lines—i. e., the purest and most monochromatic sources—are desirable. Of secondary importance are the brightness and ease of production and isolation of such sources. At moderate intensity, sodium yellow is pure only to 1 part in about 700; mercury green, to 1 in 10,000; cadmium green, to 1 in 100,000; helium yellow, to 1 in 200,000, or to 1 in 15,000 if the satellite is included. Obviously such lines are ill adapted to serve as pure sources or absolute standards.

But these are all composite lines. There is an abundance of normal lines, easily produced in arcs, whose impurity at moderate intensity is less than 1 in 100,000 in open air, and 1 in 1,000,000 at low pressures. It would appear to be in the highest degree advisable if attention were confined to these normal lines when very pure sources are desired. Work with the Michelson or Fabry-Pérot interferometers is particularly liable to error on account of the ease with which impurities may be overlooked and ignored.

I had hoped to find normal lines varying widely in minimum width and intensity coefficient, in order that the narrowest and least variant might be selected as standards and monochromatic sources. That there is so little diversity means that greater experimental skill must be exercised in producing the source, but gives a wide range of available lines.

BUREAU OF STANDARDS,
Washington, D. C.,
July 1906.

PLATE II



PHOTOGRAPHS OF ARC SPECTRA

PHOTOGRAPHS OF CERTAIN ARC SPECTRA FROM λ 5800 TO λ 8500

By LORD BLYTHSWOOD and WALTER A. SCOBLE

In order to make a practical test of the diffraction gratings cut on the Blythswood dividing engine, photographs of a number of arc spectra were taken, using a concave grating of ten feet radius. At the same time it was desired to work so far as was conveniently possible into the ultra-violet and infra-red. As the total length photographed was about forty inches, two exposures were made, dyed films being used for the red end. Experiments were made to determine the relative values of various dyes for this purpose, alizarine blue *S* being found the best and pinacyanol next. When an attempt was made to dye the films with alizarine blue for the spectrum photographs, using Mr. Higgs' formula, they were found to be very capricious, only about one film in four being satisfactory. The same result was noticed by General Waterhouse, who discovered the dye. It was therefore decided to use pinacyanol. Further experiments have since indicated a new method with alizarine blue which appears to be quite certain, as a large number of exposures have been made without a single failure. The pinacyanol films have photographed to λ 7500 and alizarine blue films to λ 8750. The photographs given here were taken to extend the range beyond that of the original pinacyanol films.

Since the lines in the added region are comparatively few in number, a concave grating of 37.6 inches radius was employed to produce the spectrum. The slit was placed at the center of curvature of the grating, and a film-holder, cut with a radius half that of the grating, was fixed in a suitable position on the circle having the line from slit to grating as diameter. The arc was usually produced by feeding the element examined, or one of its salts, into a carbon arc, the carbons being held in an ordinary hand-regulated lamp with a side adjustment. The carbons were of the usual commercial kind, which were found to compare favorably with those specially prepared. The

[1] *Photographic Journal*, May 1906, "The Red Sensitiveness of Dyed Films."

arc was on a 100-volt circuit with a resistance in series, no higher voltage being available. An image of the arc was formed on the slit. To screen out the second-order violet and ultra-violet a glass cell containing a solution of potassium bichromate was placed in front of the slit. This arrangement had the advantage that the definition is unimpaired, as the screen was not between the slit and film. The strength of the solution was adjusted by using a wide slit and an arc strong in violet light. The grating was viewed directly and the strength of the solution increased until all the violet light was cut out. A test exposure was made to confirm the efficiency of the screening and the final photographs justified it.

The films used were Wellington orthochromatic, dyed as follows: To 100 cc alcohol add 2 cc strong ammonia and dissolve 0.2 gram alizarine blue *S*. Add 100 cc distilled water and filter. The bath was used immediately after it was prepared. The films were washed for two minutes in a one per cent. solution of ammonia and dyed for two minutes, then washed for an equal time in running water. The films only keep for about a day after dyeing, consequently they were exposed wet, clamped to the film-holder. To obtain good results the staining bath should be green, regularly obtained as above. The alcohol apparently causes the film to take the dye.

The films were developed with hydroquinone applied by means of a brush, thus allowing a considerable amount of control. The usual exposure was about one hour. A fact which caused the development to be rather difficult was that the density of the developed image could not be judged by the surface. When the surface is faint it frequently happens that the true image, as seen by the faint transmitted light obtainable in the dark room, is very dense. Sometimes when nothing is visible on the surface, or even by transmitted light, after fixing a considerable image is seen. This effect is not serious if the exposure has been sufficient, but is liable to cause dense parts to be overdeveloped. A deep green light was employed in the dark room.

A scale was drawn and prints from it placed against the photographs. Under these conditions the scale serves to indicate the positions of the lines approximately, but errors are sure to occur. In cases in which lines of known wave-length appear in the infra-red,

corrections can be applied. The following treats of the spectra separately:

Lithium.—Material: lithium chloride in carbon arc; impurities: sodium and potassium .

Sodium.—Material: sodium carbonate in carbon arc; impurities: lithium and potassium. Second-order potassium lines appear faintly at λ 8089 and 8095. There is a double line at λ 9000.

Potassium.—Material: potassium carbonate in carbon arc; impurities: sodium, lithium, calcium, and silicon.

Calcium.—Material: calcium chloride in carbon arc; impurities: sodium and lithium.

Strontium.—Material: strontium chloride in carbon arc; impurity: sodium.

Barium.—Material: barium chloride in carbon arc; impurity: sodium.

Cadmium.—Material: cadmium bromide in carbon arc; impurities: potassium and sodium.

Chromium.—Material: chromium metal in carbon arc.

Manganese.—Material: manganese chloride in carbon arc; impurities: sodium and lithium.

Iron.—Material: arc between metal rods. Faint lines appear at λ 8030, 8085, 8120, 8265, 8385, 8440, on the scale.

Cobalt.—Material: cobalt chloride in carbon arc; impurity: sodium.

Nickel.—Material: nickel chloride in carbon arc; impurity: sodium.

Copper.—Material: cupric chloride in carbon arc; impurity: sodium.

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Renfrew, N. B.

Minor Contributions and Notes

THE MIDNIGHT ILLUMINATION ABOVE THE NORTHERN HORIZON NEAR THE TIME OF THE SUMMER SOLSTICE

This summer I have made observations of the illumination under the pole at midnight, near the summer solstice. This phenomenon was seen by Professor Newcomb from high altitudes in the mountains of Switzerland in the summer of 1905.[1] There were but few nights on which it could be well seen here this summer. It was satisfactorily observed, however, in particular, on the night of June 22. Careful observations show that the light is far more extensive than my casual recollections of it would imply[2]; and, unless the generally accepted ideas of the extent of our atmosphere, or the effect of the Sun in illuminating it at great altitudes, are entirely wrong, the illumination must be a manifestation of the zodiacal light, as suggested by Professor Newcomb.

1906, June 12. At midnight there was a distinct glow under the pole which reached 8° above the horizon and beyond. This glow was very diffused and extended for many degrees to the west, and to the Milky Way in the east. Near the horizon elsewhere the sky was dark.

Following are the observations made on the night of June 22 of this year.

$11^h\,0^m$. The twilight glow is noticeable to the left of the north point.

11^h30^m. It is easily seen as high as one-third the distance to *Polaris*, and is as conspicuous as the Milky Way between *Cassiopeia* and *α Cygni*. The limit of its visibility to the west would be on a vertical through *β Ursae Majoris*. The eastern limit is lost in the Milky Way. The light is conspicuous. It is a soft pale glow. In the past half-hour its motion to the right has been noticeable. It can easily be traced half-way to *Polaris*, and by averted vision diffuses even farther than that. The light is very soft and diffused with no definite limits. The sky elsewhere, which is unusually clear after several days of cloud and rain, is dark.

$12^h\,0^m$. The glow is so decidedly visible that one would not fail to notice it if looking toward the northern sky.

$13^h\,0^m$. The brightness has now passed to the right of the north

[1] *Astrophysical Journal*, **22**, 209, 1905.

[2] *Ibid.*, **23**, 168, 1906.

point. The glow diffuses nearly to *Polaris*. It is easily seen half-way to *Polaris*, and gradually fades farther than this. To one-third the distance to *Polaris* it is very noticeable.

$13^h\ 40^m$. It is now away to the right of the north point; *Capella* is in a strong dawn, which extends 10 ° or 20° above and to the left of that star. The western limit would have the same azimuth as α *Ursae Majoris*. I have watched this illumination at frequent intervals tonight, and have seen it pass under the pole and move to the east. The sky is fine except near the horizon.

$14^h\ 0^m$. The sky is now getting bright everywhere in the region of *Capella*, and the glow is widening and rising—true dawn is approaching. On this night both Mr. Barrett and Mr. Sullivan, who were working in the 40-inch dome, confirmed the observations.

June 28. The illumination passing under the pole, was visible all night.

July 17, $11^h\ 30^m$. The illumination under the pole well seen to one-third the distance to the pole. At 12, haze all over the north prevented observations of the illumination.

It would seem, therefore, if this is the zodiacal light, that it extends at least 65° north and south of the Sun (assuming the southern extent to be the same as the northern), which is a considerably greater extent than that given it by Professor Newcomb.

E. E. BARNARD

YERKES OBSERVATORY,
August 2, 1906

LATITUDE AND LONGITUDE OF THE SOLAR OBSERVATORY[1]

Through the courtesy of Superintendent O. H. Tittmann, of the United States Coast and Geodetic Survey, the astronomical latitude and longitude of Mount Wilson were determined in December 1905 and January 1906 by Assistants Edwin Smith and John E. McGrath, of the Survey. I am indebted to Superintendent Tittmann for the following information regarding the observations.

The latitude observations were made on three nights—December 24 27, and 29, 1905. Forty-six observations were taken on sixteen pairs. The observations were made with meridian telscope No. 3, having a focal length of 80 cm and a clear aperture of 7 cm. The value of one 2-millimeter division of its latitude level is $1''.186$, and the value of one turn of the eyepiece micrometer, as determined from the latitude observations at this

[1] *Contributions from the Solar Observatory*, No. 9.

station, is 65″.034. The probable error of a single observation, as derived from the residuals of the separate observations on each pair from the mean result for that pair, and, therefore, not including the errors of the star places, was found to be ±0″.36. The mean result from each pair is given in Table I. The star numbers, as given in this table, refer to the *Greenwich Ten-Year Catalogue* of 1880, with the exception of the two numbers which are inclosed in parentheses; these refer to the *Greenwich Ten-Year Catalogue* of 1890. The declinations of nineteen of the stars observed depend upon computations of mean declinations, based upon many catalogues, made at the survey office on the Boss system in former years in connection with other latitude observations. For the remaining thirteen stars, for which sufficiently accurate declinations were not available at the Survey Office, Professor Lewis Boss kindly furnished the mean declinations from the manuscript of his *Preliminary General Catalogue*, now being prepared under a grant from the Carnegie Institution.

TABLE I

RECAPITULATION BY PAIRS OF RESULTS FOR LATITUDE (MOUNT WILSON, CALIFORNIA, 1905)

Pairs. No.	Star Nos. Gr. 10-Year 1880		Latitude	No. Obs.	*W*	*V*
1	179	191	34° 12′ 55″.10	3	15	—0″.03
2	234	(557)	55.01	3	11	+0.06
3	260	269	55.72	3	18	−0.65
4	282	321	54.83	3	16	+0.24
5	327	340	54.97	3	15	+0.10
6	362	389	54.57	3	9	+0.50
7	401	414	55.23	3	18	−0.16
8	(935)	431	55.22	2	11	−0.15
9	465	475	55.09	3	16	−0.02
10	490	500	55.62	3	16	−0.55
11	520	551	54.98	3	17	+0.09
12	557	563	54.48	3	7	+0.59
13	604	612	54.90	2	11	+0.17
14	621	662	54.57	3	13	+0.50
15	679	700	54.64	3	13	+0.43
16	719	735	55.34	3	16	−0.27

The computation of the latitude was made in accordance with Appendix 7 of the *Coast and Geodetic Survey Report* for 1898, and the weights were assigned to separate pairs by the method indicated at the bottom of page 362 of this Appendix. The weighted mean value for the latitude of the station of observation is 34° 12′ 55″.07±0″.06. The reduction to sea-level to take account of the curvature of the vertical is 0″.28, making the reduced latitude of the point of observation 34° 12′ 54″.79.

The observations to determine the difference of longitude of Los Angeles and Mount Wilson were made on six nights: December 31, 1905; January 2, 3, 4, 7, 8, 1906, by Assistant John E. McGrath at Los Angeles with transit No. 19, and Assistant Edwin Smith at Mount Wilson with transit No. 18. A description of these instruments is given on page 268 of Appendix 7 of the *Report* for 1898, with an illustration opposite page 320. Each instrument has been fitted with a transit micrometer of the type described in Appendix 8 of the *Report* for 1904, "A Test of the Transit Micrometer."

The difference of longitude Los Angeles—Mount Wilson is the first one wholly within the United States determined by using transit micrometers. Earlier in the season the transit micrometers were used in observations to determine three differences of longitude fixing three points in Alaska. The observations on each night at Los Angeles and Mount Wilson consist of two time sets, each involving ordinarily twelve stars; one time set being taken before the exchange of signals between stations by telegraphy, and the other afterward. The observed differences of longitude on each night are shown in Table II, together with the residuals, the mean and its probable error.

TABLE II

DETERMINATION OF DIFFERENCE OF LONGITUDE OF TRANSIT INSTRUMENTS AT LOS ANGELES AND MOUNT WILSON, CALIFORNIA

Date	Difference of Longitude	Residual
1905, Dec. 31	$0^m\ 47^s.580$	$-0^s.009$
1906, Jan. 2	.601	− .030
3	.561	+ .010
4	.608	− .037
7	.532	+ .030
8	.544	+ .027
	Mean = $+0^m\ 47^s.571 \pm 0^s.008$	

The longitude of the transit of 1892 at Los Angeles is $7^h\ 53^m\ 01^s.561$, fixed by the adjustment of the longitude net of the United States, see Appendix 2 of the *Report* for 1897. The transit used by Assistant John E. McGrath was $0^s.140$ west of the transit of 1892, and its longitude was, therefore, $7^h\ 53^m\ 01^s.701$. Applying to this the measured difference of longitude, as given in Table II—namely, Mount Wilson transit east of Los Angeles transit $47^s.571$—there is obtained as the longitude of the transit at Mount Wilson $7^h\ 52^m\ 14^s.130 = 118°\ 3'\ 31''.95$.

The transmission time, as determined on different nights, varied from 0ˢ.003 to 0ˢ.010, with a mean of 0ˢ.007.

The local triangulation at Mount Wilson, done by Assistant Edwin Smith, shows that the Mount Wilson triangulation station is 4″.93 north and 13″.59 west of the Mount Wilson longitude station, and that the Snow Telescope Pier is 4″.74 north and 2″.94 west of the Mount Wilson longitude station. Hence the astronomical position transferred to each of these points is as follows:

MOUNT WILSON TRIANGULATION STATION

Latitude	34° 12′ 59″.72
Longitude	118 3 45.54

SNOW TELESCOPE PIER

Latitude	34° 12′ 59″.53
Longitude	118 3 34.89

By comparing the astronomical latitude and longitude, as given in this report, with the geodetic position of the Mount Wilson triangulation station on the United States Standard Datum, as printed on page 541 of Appendix 9 of the *Report* for 1904, "Triangulation in California," it is found that the astronomical latitude is 26″.50 less than the geodetic, and the astronomical longitude is 5″.63 greater than the geodetic. The deflection in the prime vertical at the Mount Wilson longitude station is therefore moderate in magnitude, but the deflection in the meridian is very large; one of the largest, if not the largest, yet observed in the United States.

I take pleasure in extending the hearty thanks of the Solar Observatory to Superintendent Tittmann, and to Messrs. Smith and McGrath, for their kindness in undertaking this work, which was carried out with the precision and dispatch characteristic of the Coast and Geodetic Survey

GEORGE E. HALE.

MOUNT WILSON, CALIFORNIA,
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